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THE RIPENING OF PEACHES.[1]

BY W. D. BIGELOW AND H. C. GORE.

Received June 3, 1905.

AT THE meeting of the Association for the Advancement of Science in December, 1903, the writers contributed an article on "The Ripening of the Apple." The present work is a continuation of a series of studies begun at that time. The methods employed in the study of the apple have been also applied to the study of the peach. The literature relating to the composition of the peach is very limited. The majority of the analyses that have been reported were made by old methods and are not to be credited for that reason at the present time. Of the analyses made according to modern methods but two are at all complete.[2]

For this work the writers had exceptional opportunities to secure a wide range of varieties of peaches grown under similar and well-known cultural conditions. The varieties were selected and secured by Mr. William A. Taylor, Pomologist in Charge of the Field Investigations of the Department of Agriculture. The work was so planned that the fruit of each tree of the varieties selected

[1] Read before the Association for the Advancement of Science, December 27, 1904.

[2] Kulisch: *Z. angew. Chem.*, 1894, p. 148, and Girard Bull. [Min. Agr. France], 1898, **17**, No. 7, p. 1523.

was sampled as carefully as possible at each picking. The examinations were made at three—and when possible, at four intervals of the life history of the peach. The times selected for the sampling were definite stages in the development of the fruit. They were as follows:

(1) *After the June drop.*—This period of the life history of the peach was selected as the first time of sampling because of the fact that it is the earliest point at which a sample can be secured of the fruit that will probably mature normally. The fruits which are not going to mature on account of imperfect fertilization or other cause, "shatter" or drop off at this time. Before securing the first sample, the trees were shaken and a portion of the fruit, which appeared to be firmly attached, selected from different sections of the tree was picked.

(2) *When the stone hardens.*—The peaches were carefully watched until the time when the stone could only be cut through with difficulty with a knife. The second sample of peaches was then secured.

(3) *When market ripe.*—Here the fruit is fully developed and almost the full degree of color has been attained. The flesh, however, is firm and the fruit will stand shipping. This is the commercial picking time.

(4) *When fully ripe.*—Here the peach is fully colored and somewhat larger than at the time of market ripeness. The flesh is soft and the fruit so easily bruised by handling that it will not stand shipment.

As stated before, in selecting all the samples the fruits were gathered from all sides of the tree and from the inner as well as the outer portions. In all cases the samples taken for analysis were of such size as to preclude, as far as possible, individual irregularities of composition. An attempt was made to secure a sample of such size that its composition would represent the composition of the average peach upon the tree at that time. Of the first samples picked about a hundred peaches were employed. Of the last samples, when the peach was fully ripe, about twenty peaches of each variety were secured for each sample. The fruit was gathered by one of us on the morning of the same day on which the analysis was begun. The varieties of peaches employed were Triumph, Rivers (or Early Rivers), Early Crawford, Stump (or Stump the World), Elberta, Orange Smock and Heath Cling (or

White Heath). The following characteristics of the varieties are taken from the description furnished by Mr. W. A. Taylor, through whom the peaches were secured. The complete description will be published in the bulletin from the Bureau of Chemistry in which the final full report of the work will be given. The Triumph is a soft-fleshed, semi-cling peach, little esteemed except for its extreme earliness. Its flesh is yellow, stained with red, firm, somewhat fibrous, juicy and mildly sub-acid. It is chiefly used for eating out of hand or for slicing.

The Rivers is a delicate fleshed, soft, easily bruised, semi-cling peach, chiefly prized for its earliness and productiveness. Its size is small to medium. Its flesh is greenish white, tender, melting, juicy and sub-acid.

The Early Crawford is a large freestone with yellow flesh stained red at stone. It is tender, melting, juicy, rich and sub-acid. It is highly esteemed for use in the fresh state and for canning.

The Stump is a medium sized freestone with white or greenish white flesh stained red at the stone. The flesh is tender, melting, moderately juicy, sub-acid. It is highly esteemed for canning.

The Elberta is a large freestone with yellow flesh stained red at stone. It is meaty, tender, moderately juicy and sub-acid. It is chiefly esteemed for its uniform large size, bright color and good shipping quality. It is a fairly good canner, but not highly esteemed as a dessert peach. As a commercial variety it is the most popular at the present time in the middle states and in southern peach districts.

The Orange Smock is a medium-sized freestone with light yellow flesh red at stone. The flesh is melting, moderately juicy and tart. Its season is late. It is used for canning and drying rather than in the fresh state.

The Heath Cling is of moderate size. Its flesh is creamy white and firm, melting, juicy, sweet and rich. Its season is very late. On account of its firm flesh and fine flavor it is popular for canning and preserving.

The fruit was grown on the farm of Mr. M. B. Waite, at Woodwardville, Md., in the summer of 1904. The season was abnormal. For six weeks prior to August 10th the atmosphere was very humid, resulting in the ruin of all peaches ripening up to that date. The rainfall then ceased and by August 20th the season became abnormally dry. No rain fell after that date until the latest of the

peaches were gathered. In comparing the ripening of the early and late peaches with each other, therefore, the varying climatic conditions to which the two classes were subjected must be taken into consideration. The fruits of the first two pickings were examined microscopically for starch. No starch was found in the embryo or in the stone, and none in the flesh with the exception of a thin layer of granules just under the epidermis of the fruit. The specimens which apparently had the largest amount of starch were examined quantitatively and 0.1 per cent. found to be present. This amount is, of course, negligible and no further determinations of starch were made.

The changes in composition of growing substances may be considered from two standpoints: First, the percentage composition of the substance at various stages of growth, showing the change in composition of the substance and hence the change in nature as it progresses. Second, from the standpoint of the actual weight of solids, water, starch, sugar, proteids, etc., in an individual of the species under examination. Obviously, the actual weights of each ingredient present in each peach at various stages of the life history of the fruit are of much greater interest and throw much more light on the changes in chemical composition than does the analysis of the peach itself without reference to its weight at different periods in its life history. Unfortunately, this matter has not always been given sufficient consideration in studying the ripening of fruits. In only two cases (Elberta and Orange Smock) were the peaches examined fully ripe. This is because it was impossible to preserve samples on the tree until they became fully ripe. In addition to the dropping of the peaches which would normally take place, the orchards were somewhat afflicted with *scab*, which increased the tendency of the peaches to drop.

The change in composition between the time of the hardening of the stone and the time of market ripeness is very great. During this period the weight of the peach is increased more than fourfold. The proportion of flesh to stone increases about seven times and the composition of the flesh itself goes through much greater changes than earlier in the life history of the fruit. The examination of samples at more frequent intervals would shed greater light on the life of the peach at the times when these changes begin and when they are greatest and for that reason would be valuable. The results here given are believed to be of value in that they mark

out the boundaries within which certain changes occur and limit the field in which further investigations of this nature can be carried on with profit. Taken in connection with the results given, a smaller amount of work will be necessary to accumulate details to make our knowledge of the life history of the peach much more complete than it is at present. We give here only the summaries of the various tables of analyses, showing the average change in composition of the six varieties of peaches studied.

Between the time of the June drop and the period of market ripeness the peaches increased in weight on an average of from 9.51 to 73.59 grams per peach. The percentage of flesh in the peach increased from 64.55 to 92.49, that is, the weight of the fleshy portion of the peach increased more rapidly than the weight of the stone. At the time of the June drop the stone constituted 32.5 per cent. of the weight of the entire peach, whereas, at the time of the market ripeness it constituted but 6.86 per cent. of the weight. The percentage of solids in the flesh of the peach remained fairly constant during its life history; that is, the increase in solids is fairly proportionate to the increase in water. On the other hand, the stone changes gradually in its nature. As it becomes harder and more mature the percentage of water decreases. The same is true of the embyro; that is, the solid content gradually increases with the maturity of the peach.

As has been stated before, absolute changes, as distinguished from relative changes in the composition of the growing fruit, can only be determined from the expression of the results in terms of grams per individual. In Table II is given the average composition of the six varieties of peaches examined in terms of grams per peach. It is apparent that the flesh of the peach increases rapidly, amounting to eleven times from the date of the June drop to the period of market ripeness. On the other hand, the increase in the weight of the stone is apparently small. The embryo almost doubles its weight between the time of the June drop and the hardening of the stone and after that its weight does not appreciably change. Since, as we noted in Table I, the amount of solids and water in the flesh of the peach (as percentage) remained practically constant the increase in the weight of the solids must be proportionate to the increase in weight of the flesh of the peach. This we find to be true in Table II. The solids increase from the 0.903 gram per peach at the time of the June drop to 9.719 grams at

the time of market ripeness. This is in keeping with the observation previously made that the percentage of solids in the stone increases while the weight of the stone remains practically constant throughout the life history of the peach. The weight of the solids in the embryo increases in somewhat the same proportion as the weight of the solids in the stone. It is also apparent that the decrease in marc (apparent in Table I) between the second and third periods at which the fruits were examined is relative and not absolute, since the weight of the marc in grams per peach is almost doubled between the time of the hardening of the stone and the period of market ripeness. The weight of the reducing sugar increases almost eight times between the time of the June drop and the time of market ripeness, and the increase in sucrose and acids is far greater than that of reducing sugar. The various forms of nitrogenous substances all increase in weight from the beginning to the end of the period of observation. There is no apparent tendency for proteids to be decomposed into simpler nitrogenous bodies or to be built up from the simpler forms in the growth of the peach. On the other hand, the relation between the amount of amido bodies and proteids is fairly constant throughout.

As was stated before, in some of the varieties under examination the peaches dropped from the trees before any of them became fully ripe. Samples of three varieties in the fully ripe state were, however, secured. In Table III the average composition of the three varieties is given in terms of grams per peach, both in the market ripe state and at the period of full ripeness. From an examination of this table it is apparent that a peach has not nearly reached its full weight at the time of market ripeness and that its increase in weight is due, not to increase in water content alone, but also to increase in solids. Both reducing sugar and sucrose increase during this period. On the other hand, the absolute increase in marc is considerably decreased and also that of acids.

An attempt was also made to determine the change of composition in peaches picked at the time of market ripeness and preserved in cold storage. Owing to the rapid deterioration of the peaches in storage, however, the results of the study of the influence of storage on their composition were not nearly as satisfactory as were obtained in the study of the influence of storage on the composition of apples. Unfortunately, the fact that we cannot store peaches for any great length of time after ripeness prevents us

from ascertaining whether, after full maturity and especially after picking, sucrose ceases to form and whether when formed it is converted into reducing sugar as is the case in the apple. The sucrose content of the apple increases after picking, owing to the hydrolysis of starch, and after the starch has entirely disappeared the sucrose content of the apple decreases owing to inversion. The peach has practically no starch at any period of its growth and after picking, the sucrose content does not increase. There appears to be a tendency toward the inversion of sucrose, but this is not nearly so marked as in the apple.

TABLE I.—PERCENTAGE COMPOSITION OF PEACHES.

(Average of six varieties.)

Time.	After June drop.	Hardening of stone.	Market ripe.
Average weight, grams....	9.51	16.75	73.59
Per cent. flesh.....	64.55	71.54	92.49
Per cent. stone.....	32.50	25.82	6.86
Per cent. embryo.....	2.94	2.89	0.65
Per cent. solids in stone...	9.37	27.35	66.94
Per cent. solids in embryo.	6.89	7.54	44.78
Analysis of flesh.			
Per cent. solids.....	14.77	16.97	14.04
Per cent. marc.....	7.37	7.71	2.51
Per cent. reducing sugar ..	2.71	2.26	1.98
Per cent. sucrose.....	0.18	1.57	5.70
Per cent. acid as H_2SO_4....	0.28	0.34	0.56
Per cent. nitrogenous bodies	0.98	0.81	0.35
Per cent. albuminoids[1]....	0.77	0.63	0.27
Per cent. amido bodies[2]...	0.21	0.18	0.08
Per cent. ash.....	0.75	0.68	0.40

TABLE II.—COMPOSITION OF PEACHES IN TERMS OF GRAMS PER PEACH.

(Average of six varieties.)

Time.	After June drop.	Hardening of stone.	Market ripe.
Average weight, grams....	9.51	16.75	73.59
Flesh, grams.....	6.12	11.89	68.11
Stone, grams.....	3.12	4.37	5.01
Embryo, grams.....	0.28	0.48	0.47
Solids in stone, grams.....	0.29	1.17	3.18
Solids in embryo, grams...	0.02	0.04	0.21
Composition of flesh.			
Solids, grams.....	0.90	2.01	9.72
Marc, grams.....	0.45	0.90	1.74
Reducing sugar, grams....	0.17	0.27	1.37

[1] By Stutzer method—albuminoid nitrogen, times 6.25.

[2] Amido nitrogen, times 4.25.

Time.	After June drop.	Hardening of stone.	Market ripe.
Sucrose, grams.....	0.01	0.16	3.94
Acid as H_2SO_4, grams.....	0.018	0.044	0.379
Nitrogenous bodies, grams.	0.060	0.099	0.181
Albuminoids,[1] grams.....	0.047	0.075	0.140
Amido bodies,[2] grams.....	0.013	0.023	0.041
Ash, grams.....	0.046	0.083	0.227

TABLE III.—COMPOSITION OF THE FLESH OF PEACHES AT MARKET RIPENESS AND AT FULL RIPENESS.
(Percentage of Total Solids.)

Serial No.	Variety.	Date. 1904.	Marc.	Reducing sugar.	Sucrose.	Acid as sulphuric.	Albuminoids.	Amido bodies.	Total nitrogenous bodies.	Ash.
				Market ripe.						
11248	Elberta.....	Aug. 25	18.71	14.42	41.85	3.34	.....	.....	.....	3.56
11295	Orange smock	Sept. 21	18.65	14.10	35.02	3.95	1.86	0.54	2.40	.....
11249	Stump.....	Aug. 25	17.70	13.04	40.77	3.24	.....	.....	.....	3.54
				Full ripe.						
11258	Elberta.....	Aug. 30	12.80	12.15	47.81	2.89	.....	.....	.....	3.28
11298	Orange smock	Sept. 26	17.05	17.49	46.07	3.37	1.82	0.374	2.19	.....
11250	Stump.....	Aug. 25	12.96	12.50	43.04	2.60	.....	.....	.....	3.43
Average, market ripe.....			18.35	13.85	39.21	3.51	.....	.....	.....	.....
Average, full ripe.....			14.28	14.05	45.64	2.95	.....	.....	.....	.....

A STUDY OF DURUM WHEAT.

BY F. A. NORTON.

Received June 5, 1905.

THE Departments of Agronomy and Chemistry of this station have been carrying on an extensive investigation of the so-called macaroni wheats during the past four years.

This variety of wheat, *Triticum durum*, is largely grown in the Mediterranean regions and on the plains of Southern Russia and Siberia, also to some extent in Argentine and India. It was recently imported for trial, especially in the semi-arid parts of the middle West, by the agricultural explorers of the Department of Agriculture. In the past France and Italy have consumed the greater part of the macaroni wheat produced, the wheat being used largely in the manufacture of macaroni, but to some extent as a

[1] By Stutzer method—albuminoid nitrogen, times 6.25.
[2] Amido nitrogen, times 4.25.

bread wheat. If adapted to our soil and climate it was thought that these wheats might afford a cereal for the areas of low rainfall of this country; that they might stimulate the manufacture of macaroni in the United States and enable us to compete with other countries in the supply of durum wheats to France and Italy.

The work of this station has been in collaboration with that of other stations and the Department of Agriculture to ascertain the adaptability of these wheats to this country. The Department of Agronomy has carried on field tests and cross-breeding work with nearly one hundred different samples, representing all the important varieties of the durum wheats. The cross-breeding work has not yet developed any important modifications, but the field tests have demonstrated their adaptability for the more arid portion of this and neighboring states. In those portions of the state having an annual rainfall of twenty inches or more, results have been less gratifying, though the macaroni wheats seem to be more rust-resistant.[1]

The Department of Chemistry of this station first took up nitrogen control investigations to determine whether the high protein content would persist under our climatic and soil conditions, and later took up milling, bread and macaroni tests. The milling tests were made by Prof. J. H. Shepard, who has had the direction of the chemical work. The nitrogen control determinations and determinations for nitrogen content of the mill products have been made by Mr. Hepner, now connected with the Wyoming station. The bread, macaroni and gluten tests have been the work of the writer, also the color determinations and other work recorded in this paper.

The Wheat.—The durum wheats have a very large kernel, the grains being nearly twice as large as those of the ordinary bread wheats. They are hard, of an amber color, and, when plump, appear almost translucent; they yield well and grade heavy, the yield usually being from one-third to one-half more than that of the best bread wheats. The drought-resistant qualities are shown by the crop of 1903, grown at the substation at Highmore, S. Dak.,[2] where the rainfall for the year was only fifteen inches. The average yield for all of the durum wheats grown at the substation that season was 14.7 bushels per acre, while the maximum yield was

[1] Lessons from Grain-rust Epidemic of 1904, Farmer's Bulletin, No. 219. U. S. Dept. of Agr.

[2] Report of Investigations at Highmore Substation for 1903, Bulletin No. 84, S. D. Expt. Station.

20.2 bushels per acre, and several of the best wheats gave a yield of from 18 to 20 bushels. The bread wheats the same season and at the same place produced only 4 or 5 bushels per acre. The durum wheats were of excellent quality, five of the best of the crop of 1903 giving an average grade of 62.3 pounds per bushel, while five bread wheats of exceptional quality, such as Fife and Blue Stem, milled for control, in the milling, bread and macaroni tests, graded only 59.9 pounds per bushel.

Mill Products.—The milling tests were made on a miniature Allis-Chalmers mill, provided with corrugated and smooth rolls and bolting arrangement. Power was furnished by a gasoline engine. No middlings purifier was used and the mill products were separated only into bran, shorts and straight flour.

Reduction was first made on the corrugated roll and completed on the smooth roll. That portion which remained on a 30-mesh sieve after complete reduction was taken off as bran. The portion passing through a 30-mesh sieve, but remaining on a No. 12 bolting-cloth, was returned as shorts, while the portion passing through the cloth was taken as the flour yield. These conditions gave very satisfactory results for total flour yield and would compare favorably with commercial milling for straight flour.

There were very marked differences as to the milling properties of different wheats. All of the durum varieties were somewhat harder to mill than the bread wheats and some were very difficult of reduction. The Russian varieties, however, were easier to mill, possessed thinner skins and gave larger flour yields than those from the Mediterranean region or from miscellaneous sources. The following table gives the comparative yield of mill products, 500 grams of wheat being used for each quantitative milling test:

MILL PRODUCTS.

	Number of analyses.	Bran. Per cent.	Shorts. Per cent.	Flour. Per cent.	Error. Per cent.
Macaroni wheats.....	45	20.48	17.93	61.60	+0.01
Bread wheats.....	5	20.40	10.56	68.56	—0.48
Best Russian wheats[1]	5	15.91	16.25	67.60	+0.24

Proximate Analysis.—In order to determine more definitely the general composition of the durum wheats as compared with the bread wheats, a proximate analysis of one of the best Russian wheats (Kubanka 5639) and one of the best bread wheats (Blue Stem, Minnesota, No. 169) was made. The determinations were

[1] Kubanka, Pererodka, Arnanka, Beloturka, and Yellow Gharnovka which will be referred to on other occasions as the five best durum wheats for the Great Plains Region.

carried out in duplicate according to the Official Methods of the Association of Official Agricultural Chemists.[1] In the following table may be found the results of the analysis, together with the mean of domestic wheats, as published by the Bureau of Chemistry of the Department of Agriculture:[2]

PROXIMATE ANALYSIS.

	Kubanka. Per cent.	Blue Stem. Per cent.	Mean of domestic wheats. Per cent.
Moisture	9.32	6.00	10.62
Ash	1.71	2.46	1.82
Fat or ether extract	2.34	2.49	1.77
Crude fiber	2.52	3.35	2.36
Crude protein, N×5.7[3]	14.46	13.21	12.23
Carbohydrates other than crude fiber	69.65	72.49	71.18

Soluble Carbohydrates.—On account of the sweetness of the macaroni wheat products determinations of dextrine and sugar were made on Kubanka 5639, and of sugar on Blue Stem, Minnesota, No. 169. The method of the Association of Official Agricultural Chemists[4] was used for the sugar determination, with the exception that after inversion the sugar was determined by the Defren-O'Sullivan method,[5] the sugar being calculated from the cupric oxide by the factor 0.4307. As thus determined, the Kubanka gave 3.26 per cent. of sugar and the Blue Stem 1.42 per cent., invert sugar and soluble starch being absent in both wheats. Dextrin was determined according to the Stone method[6] and a content of approximately 1.25 per cent. was found for Kubanka. There are not many sugar or dextrin determinations on wheats recorded. Villier and Collin, however, in their summary of cereal products, give the sugar content of whole wheat as 1.45 per cent., while Stone[6] reports 0.52 and 0.72 per cent. of sucrose, and 0.27 and 0.41 per cent. of dextrin on two whole wheats analyzed. This would indicate a much higher sugar and dextrin content for the durum wheats than for the bread wheats.

Flours carry somewhat less sugar than the whole wheat. Stone[6] records 0.18 and 0.20 per cent. on two samples of flour analyzed, while determinations by Krug and Wiley[7] would show that 0.3

[1] Bulletin No. 46, pp. 23–24, Bureau of Chemistry, U. S. Dept. of Agr.

[2] Bulletin No. 13, Part 9, p. 1186, Bureau of Chemistry, U. S. Dept. of Agr.

[3] For use of N × 5.7 see Bulletin 13, Part 9, p. 1191, Bureau of Chemistry, U. S. Dept. of Agr.

[4] Bulletin No. 46, p. 24, Bureau of Chemistry, U. S. Dept. of Agr.

[5] This Journal, **18**, 749.

[6] Bulletin 34, Office of Experiment Stations, Dept. of Agr.

[7] Bulletin 13, Part 8, Bureau of Chemistry, U. S. Dept. of Agr.

per cent. is the maximum for most bread wheat flours. However, corrections necessary in the gliadin determinations would indicate that the macaroni wheat flours contain from 1 to 2 per cent. of sugar as sucrose.

Protein Content and Nitrogen Control.—The protein content of durum wheats is very high and as wheats have been shown[1] to be extremely susceptible to changes of soil and climate in regard to this most important constituent of wheats, as concerns food and milling values, nitrogen determinations have been made each year on the whole wheat to ascertain whether the protein content would persist under our soil and climatic conditions.

In the following table the trend of the protein content is shown, the results being calculated to the water-free basis:

PROTEIN CONTENT.

	Number of analyses.	Protein, N × 5.7. Per cent.
Imported seed	7	15.73
Crop of 1901	31	18.13
Crop of 1902[2]	32	14.57
Crop of 1903	45	17.34

FLOUR.

Color, protein, gluten and gliadin determinations, also baker's sponge test and baking tests were made on the flour from the various wheats. For this purpose straight flour, milled by Prof. Shepard, was used, both with the bread and durum wheats.

Color.—Durum wheats possess a yellow coloring principle, which gives a more or less noticeable color to all their products. This coloring-matter, very characteristic of the macaroni wheats, might perhaps be used as a test for identity of macaroni wheat flours. The color it imparts to macaroni is used by experts as one of the criteria of quality. It gives to alcohol and ether extracts of the flour a beautiful, deep yellow color. This principle is insoluble in distilled water, but is somewhat more readily soluble in dilute alkalies than in alcohol or ether, while it is discharged from solution by acids and precipitated by lead subacetate and some other salts.

Color determinations on the flour from the various wheats gave the following results, which show the macaroni flours to have rather more color than bread wheat flours. The determinations

[1] Bulletin No. 13, Part 9, p. 1118, Bureau of Chemistry, U. S. Dept. of Agr.

[2] A very unfavorable year for macaroni wheat.

were made by means of a Lovibond tintometer and expressed in units of yellow and orange.

COLOR OF FLOURS.

	No. of tests.	Yellow.	Orange.
Bread wheat flours	5	0.18	0.05
Durum wheat flours	45	0.25	0.17
Best durum wheat flours	5	0.25	0.11
Patent macaroni wheat flours[1]	2	0.20	0.10

Protein.—The protein content of the durum wheat flour, as milled, in all cases approximated very closely to that of the whole wheat. The following table will give a comparison between the flours of the durum and the bread wheats.

PROTEIN CONTENT OF FLOUR.

	No. of analyses.	Protein air-dry. Per cent.
Bread wheat flours	5	12.66
Macaroni wheat flours	45	15.00
Best Russian wheat flours	5	14.51
Mean of domestic flours[2]	..	9.30

It is evident from the above that the protein content of the macaroni wheat flours is considerably larger than that of the bread wheat flours, and a simple calculation from the mill products and protein content shows that five of the best durum wheat flours contain 10.08 pounds of protein in 100 pounds of flour as against 8.69 pounds of protein in 100 pounds of flour from the five bread wheats milled.

Gluten.—The amount and quality of the gluten has a very important bearing upon a flour as to bread-making qualities. In all the durum wheats the gluten content is large, but the quality is not as good as that of the bread wheat flours. The gluten of many of the flours showed very poor adhesive qualities and was, with difficulty, collected on washing out the starch in the gluten tests. It also seemed lacking in elasticity, both of which characteristics would indicate a deficiency of gliadin. The gluten determinations were made by the method outlined by Wiley.[3] The results with the mean given by Wiley[4] for American wheat flours follow:

[1] One milled by Farmer's Mill and Grain Co., Milnor, N. D., and the other by the Brookings Roller Mill, Brookings, S. D.

[2] Bulletin No. 13, Part 9, Bureau of Chemistry.

[3] "Principles and Practice of Agricultural Analysis," Vol. III, p. 435.

[4] Bulletin No. 13, Part 9, p. 1186, Bureau of Chemistry, U. S. Dept. of Agr.

GLUTEN CONTENT.

	No. of determinations.	Moist gluten. Per cent.	Dry gluten. Per cent.	Water held by 1 gram dry gluten. Grams.
Bread wheat flours.....	5	45.99	14.82	2.10
Macaroni wheat flours.....	45	53.77	17.68	2.04
Best macaroni wheat flours.	5	51.20	16.94	2.02
Macaroni patent flours.....	2	48.40	13.38	1.87
Mean for domestic flours		26.50	10.25	1.58

Gliadin in Flour.—Osborne and Voorhees have shown the importance of this proteid and state[1] that upon it the formation of the gluten largely depends. Snyder emphasizes the same point and suggests[2] that a flour to possess good bread-making qualities should contain 11 per cent. of protein (N×5.7) and that from 55 to 65 per cent. should be in the form of gliadin. Snyder also states[3] that while poor bread-making qualities may be due to other causes than either an excess or a deficiency of gliadin, that it is, however, due more frequently to an unbalanced condition of the gluten than to any other cause. Fleurent[4] gives the limits of gliadin as 32 to 60 per cent. of the gluten, which constitutes from 85 to 90 per cent. of the total proteids and states that when there is an excess of glutenin and consequently a deficiency of gliadin the dough neither rises during the fermentation nor in the oven, and the bread is heavy and indigestible. This is the case of the bread made from many of the poorer durum wheat flours, and hence the gliadin determinations are of special interest.

The determinations were made by the method recently proposed by Snyder.[5] However, it was necessary to precipitate the gliadin with mercuric nitrate and make corrections for sucrose, which has been shown to be present in considerable quantity in the durum wheats. The corrections varied from 0.7 to 1.8 per cent. on the sugar scale of a Schmidt and Haensch polariscope. The results on ten durum flours are summarized below:

GLIADIN DETERMINATIONS—WATER-FREE BASIS.

	Gliadin nitrogen. Per cent.	Gliadin N×5.7. Per cent.	Gliadin of total protein. Per cent.
Maximum.....	1.51	8.61	50.00
Minimum.....	1.04	5.93	35.74
Average five best durum wheats....	1.38	7.87	47.17

[1] "The Proteids of the Wheat Kernel," pp. 78–79.
[2] This Journal, **26**, 266.
[3] Bulletin No. 85, Minn. Expt. Sta.
[4] Manual l'Analyse Chimique, 1898, pp. 308–314.
[5] Bulletin No. 85, Minn. Expt. Sta.

Baker's Sponge Test.—This test gives valuable information as to the water-absorption capacity of a flour and the strength of the dough, or its ability to rise. The test is made in bakeries in order to determine the value of strong and weak flours when it is desired to blend them for baking purposes. It also indicates the amount of water necessary to use for the sponge. The method[1] employed was that followed at the Minnesota Experiment Station in their work on wheats. The tests show the time required and the volume of a dough from a given amount of flour at its maximum expansion. On breaking, the dough is again allowed to rise and the results recorded are the average of the first and second rises.

BAKER'S SPONGE TEST.

	No. of tests.	Av. time of rise. Minutes.	Av. vol. of rise. cc.	Av. rise for each gram dry gluten. cc.	Water held by dough from 100 grams flour. Grams.
Bread wheat flours.....	5	80	652	44.00	77.4
Macaroni wheat flours.....	45	66	596	33.76	77.1
Best Russian wheat flours.....	5	72	670	39.45	79.1
Macaroni patent flours.....	2	64	650	48.60	76.0

The above results would indicate that the larger gluten content makes up for the poorer quality of the gluten of the durum wheats. In fact, the five best durum wheat flours give a somewhat greater average expansion than the five bread wheat flours, though the expansion for each gram dry gluten is considerably less.

Baking Tests.[2]—Macaroni wheat flour seems to have a greater tendency to hydrolyze and become sticky than bread wheat flours and must be treated more like whole wheat flour than like our best patent flours. This is true even of patent macaroni wheat flours. Also, if kneaded a little too stiff the dough does not rise properly and the bread is heavy, of poor texture, and very dark-colored. In the baking tests 300 grams of flour, 15 grams of cottolene, 10 grams of sugar, 5 grams of salt, 1 cake of compressed yeast, and water, according to the sponge test, were used. The sugar, yeast and cottolene were mixed in a porcelain dish in the amount of lukewarm water indicated by the sponge test. When the yeast became active the salt was added and flour stirred in with vigorous

[1] Annual report, 1899, p. 350, Minnesota Experiment Station.

[2] The writer is indebted to Miss Ruth Wardall, Professor of Domestic Science in the South Dakota Agricultural College, for valuable assistance in determining the best method of treating macaroni wheat flour for bread-making. Also the following studies on bread have been found very helpful: "Chemistry of Wheat, Flour and Bread, and Technology of Bread Making," Jago. "Bread and Principles of Bread Making," Helen Atwater. "Studies on Bread and Bread Making," Voorhees and Snyder. Also the later "Study on Bread and Bread Making," by Snyder.

mixing until a dough that could be kneaded was secured. The dough was then transferred to a plate glass slab and the rest of the flour kneaded in. The sponge was placed in a warm place and when it had doubled its volume was again kneaded slightly, shaped and placed in a baking-tin. When the loaf had doubled in volume it was placed in an oven at 220° C., after fifteen minutes the heat was increased to 230° to 240° C., and after fifteen minutes more allowed to fall to 200° C., forty-five minutes being required for baking. The bread was then removed from the tins and allowed to cool in free access of air. The process, as above described, usually required five hours. The volume and weight of each loaf were determined about three hours after baking, and color, texture, and flavor about eighteen hours after baking. The tests, being made on straight flours, were a severe trial of the bread-making qualities of the durum wheats, for a straight flour contains not only the first and second patents, but also the lower-grade flours, which, as pointed out by Woods and Merrill[1] and other investigators, are much darker and greatly inferior in quality of gluten. However, the tests were comparative and very satisfactory.

RESULTS OF BAKING TESTS.

	No. of tests.	Volume. cc.	Weight. Grams.	Color.	
				Yellow.	Orange.
Bread wheat flours.....	5	1630	447	0.38	0.15
Macaroni wheat flours.....	45	1480	449	0.50	0.40
Best macaroni wheat flours....	5	1580	455	0.51	0.28
Patent macaroni wheat flours..	2	1650	430	0.45	0.20

It will be seen from the above that the durum wheat breads have rather more color. All breads tend to be much darker, if not perfectly light and the macaroni breads are no exception, but, if well made and light, durum wheat breads have a fine light cream color, only slightly more pronounced than that of bread wheats. The color is pleasing and should not be objectionable to any one. In volume, weight and texture the best durum wheat breads compare favorably with those from the best bread wheats, in fact, the writer has seldom seen a much finer texture in bread than that yielded by some of the best macaroni wheat flours. The flavor of the macaroni wheat bread is decidedly pleasing and, personally, we would pronounce it superior to that of the bread from the regular bread wheat flours. On account of the higher protein content

[1] Bulletin No. 103, p. 69, Maine Experiment Station.

the breads are more nutritious and should offer a very desirable addition to the dietary of the people of the United States.

MACARONI.

Macaroni, when correctly prepared, is an excellent food and it only remains for a really first-class article to be produced, and a proper appreciation of its food value, for the consumption to be greatly increased in the United States.

Italy, and later France, have been the first countries to use macaroni to any great extent as a food. As to the increase of the consumption of macaroni in France, Robert P. Skinner, Consul-General at Marseilles, quotes[1] M. Scaramelli, an important macaroni manufacturer, as follows:

"In 1866, when I first traveled about the country selling the output of our then small factory, I once reached the village of the Grande Combe where I found that the only dealer in macaroni was the local druggist, who said that he bought 25 pounds per annum, which was sold exclusively for consumption by invalids. At the present time the same village takes 25,000 pounds of macaroni per month, which is sold to practically every family in the place. It has become a staple article of diet. In the city of Marseilles the consumption has tripled in twenty-five years."

In visiting a number of the most important factories in the United States the writer found that most of the domestic macaroni was made from bread wheat flour and that since there was a prejudice against the domestic brands most manufacturers were putting out their best grade under their own label, and their second-class goods, which constitutes the larger part of their product, under foreign labels. As a result, and also on account of the shipping and storing of the imported macaroni, a poor article is often secured and the use of macaroni tends to be discredited.

Macaroni should be manufactured from semolina, a coarse granular flour, varying degrees of fineness being used. If the semolina is crushed to a powder[2] it is so separated that what macaroni manufacturers call its "force" is lost and it makes an inferior product. The durum wheats being hard, lend themselves readily to the manufacture of semolina, while other wheats tend to go to flour, so that a much larger yield of semolina can be obtained from macaroni wheats. Another requirement is a high gluten

[1] "Manufacture of Semolina and Macaroni," Bulletin No. 20, Bureau of Plant Industry Dept. of Agr.

[2] See "Manufacture of Semolina and Macaroni," p. 25.

content. Skinner, in the bulletin quoted, places the limits at from 45 to 50 per cent. Reference to the gluten table will show that the average of the durum wheats considerably exceeds these figures.

The various paste products which go under the name of macaroni, vermicelli, spaghetti, etc., are made by mixing about 30 per cent. of water with semolina in a mechanical mixer and then kneading to a homogeneous mass by means of a powerful kneader, capable of exerting great pressure. The dough is then placed in a press and forced through a die which gives it the proper shape. It must then be dried or cured.

Soup pastes are largely dried on trays, but macaroni and spaghetti are cured either between strawboards (the French system) or on rods (the Italian system). In this country the French system is most largely used. In the work at this station the semolina used was milled by Professor Shepard. For kneading, a butter worker, which was found to give good results, was employed, while the pressing was done in a small press such as is used in the smaller Italian factories. For the curing, one of the most difficult operations, the Italian system was used, a specially arranged chamber in which heat and moisture could be controlled being constructed. The semolina, as milled, could not be entirely freed from bran particles and the kneading and pressing were not as satisfactory as with power kneaders and pressers. However, excellent samples of macaroni were made and the results of the tests were very gratifying.

The object of these tests was primarily to determine the value of wheats as raised in this country for macaroni purposes and the quality of the macaroni which the different varieties would make. At the same time macaroni was made from semolina from the bread wheats for control.

Skinner further states, in his description of macaroni manufacture, that a good macaroni should be bright, clear, semi-translucent and of a very light amber color. It should be elastic before cooking and have sufficient "force" to retain the original form after being cooked. Judging of the macaroni from the various wheats in regard to these points and also as to flavor, the macaroni from twenty-two out of forty-five durum wheats yielded a product which was graded 100 per cent., while the average of the forty-five was 96 per cent. On the other hand, the highest average quality which could be accorded a bread wheat macaroni was 85 per cent.,

and the average of the five was 82 per cent. This superiority showed itself in nearly every way. The macaroni from the bread wheats was duller and less translucent and might be described as somewhat chalky in appearance. It was also less elastic and on cooking was poorer in consistency, in fact, lacked "force." As regards flavor, the comparison was still more in favor of the macaroni from the durum wheats. Its sweetness and rich nutty flavor seem to be a quality almost entirely lacking in the macaroni from bread wheats. Miss Wardall, Professor of Domestic Science in the South Dakota Agricultural College, and various ladies favored with samples, were very enthusiastic in their praise of the durum wheat macaroni as compared with that found on the market.

Several factories, notably Fould's, of Cincinnati, and The Minnesota Macaroni Co., of St. Paul, are making an excellent quality of macaroni from durum wheats raised in this country, but it hardly seems that their process of curing, which is the French method, conserves the full sweetness and flavor of the durum wheats.

Breakfast Foods.—The durum wheats lend themselves readily to the manufacture of grits, and their high protein content, richness in sugar and characteristic and pleasing flavor, should make them a favorite for the production of breakfast foods.

The Varieties.—Little has been said so far as to the description of the varieties and individual tests which may be found in the various bulletins on macaroni wheat, published by the South Dakota Experiment Station. In general, probably on account of greater similarity in the soil and climatic conditions, the Russian wheats have given much the best results. Of these Kubanka 5639 has given somewhat the best flour yield and is one of the easiest to mill. Its yield per acre meets the average for Russian wheats, though it is excelled somewhat by several of the best wheats. It is also somewhat below the average in protein and gluten, though the gluten is of excellent quality. Kubanka, Pererodka, Arnautka, Beloturka and Yellow Gharnovka are all excellent varieties in nearly every respect and are of much the same quality. In fact, they seem to be the best varieties for the Great Plains Region.

Pellissier, the best of the Mediterranean wheats, is one of the best yielders of all the macaroni wheats. However, it gives much less flour than the Russian varieties and makes only indifferent

bread. Velvet Don and one or two others, which have been reported as especially rust-resistant, are very inferior both in respect to bread-making and macaroni, and also give a very low flour yield. Saragolla, the famous Italian macaroni wheat, has a very high protein content, but gives a low flour yield and makes poor bread, though the macaroni is of good quality.

SUMMARY.

The durum wheats are adapted for culture in many parts of the middle west, particularly in the semi-arid regions.

They yield especially well and grade high.

While many of the durum wheats are difficult of milling and give low flour yields, yet the best Russian varieties may be readily milled and compare favorably in flour yield with the best bread wheats.

The protein content, which is very much higher than that of bread wheats, tends to increase rather than diminish under our soil and climatic conditions.

They are especially rich in sucrose and dextrin.

The flour and other products have somewhat more color than those from bread wheats, due to the presence of a yellow coloring principle, but this color need not be objectionable in any of the products and is a criterion of quality in macaroni.

The gluten content is high but the gluten is of rather poor quality due to a deficiency of gliadin. However, in the best wheats the gliadin deficiency seems to be compensated for by the greater gluten content.

The best durum wheats will make excellent bread.

They are greatly superior for the manufacture of macaroni and other edible pastes, and should be well adapted for the preparation of breakfast foods.

They possess a decidedly characteristic and pleasing nutty flavor.

Of the different varieties which have been employed for trial at the South Dakota Experiment Station and Highmore substation, Kubanka, Pererodka, Beloturka, Arnautka and Yellow Gharnovka have given considerably the best results.

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THE HYDROLYTIC ENZYME—LIPASE.

By Frederick L. Dunlap and William Seymour.

Received June 7, 1905.

The first definite information concerning the existence in oleaginous seeds of an enzyme having the power of inducing the hydrolysis of oils, is due to Green[1]. The presence of such a substance had been suggested many years previously by Pelouze[2], and again, some years later, by Schützenberger[3], but it was Green who first gave conclusive proof of such an enzyme, by obtaining from the germinated castor-oil bean an extract capable of hydrolyzing oils. He likewise found that the non-germinated seed, if treated with dilute acetic acid for a time, gave an extract which was also lipolytic. His results are, for the most part, mostly qualitative, yet none the less conclusive that a hydrolytic enzyme was present in the extract.

About the same time that Green published his results, Sigmund[4] showed that when the resting rape, castor, poppy, hemp, pumpkin, maize and flax seeds are finely divided and treated with water or glycerol, an extract is obtained which, on the addition of alcohol, produces a precipitate. Sigmund found that this precipitate had hydrolytic power. There must, of necessity, be some doubt as to the quantitative value of Sigmund's experiments because he used no means of inhibiting bacterial growth.

This latter objection is not, however, applicable to the experiments of Sigmund which he published the following year.[5] In this paper, Sigmund gives results obtained with seeds in both a resting as well as a germinated condition. The resting seeds were ground with chloroform water and after twenty-four hours, the amount of acid present determined by titration. A determination of the amount of acid was made in a similar mixture as soon as prepared, the difference between the two results representing the acid formed by the lipolytic action of the lipase in the seed on the oil present, acting over a period of twenty-four hours. While the increase in the fatty acids was not marked, yet it was sufficient to warrant the conclusion that lipase was present in the seeds studied. Sigmund germinated rape, poppy and hemp seeds for two days and then dried

[1] *Proc. Roy. Soc.*, **48**, 370 (1890).
[2] *Compt. Rend.*, **40**, 605 (1855).
[3] "On Fermentation," 1876, International Scientific Series, p. 295.
[4] *Monatsh.*, **11**, 272 (1890).
[5] *Sitz. d. Kais. Akad. Wiss.* (Wien), **100**, 328 (1891).

them at a temperature of 35°. For his quantitative results, he used these dried seeds in the same fashion as the non-germinated ones, and found that the hydrolysis brought about by the germinated seeds is more intense than that developed by the resting ones. These results of Sigmund substantiate the suggestion made by Green with respect to the castor-oil bean, namely, that the lipase in resting seeds is present essentially as a zymogen, which gives rise to the enzyme during germination.

In 1898, Lumia[1] published some experimental results on the presence of lipase in germinated seeds, using for this purpose the castor-oil bean and the pumpkin seed (*Cucurbita pepo*). In the case of the castor-oil bean, the results were essentially the same as those obtained by Green, except that the intensity factor was more pronounced, for the lipase exerted its influence for a much longer period. At the expiration of six days, the increase in the fatty acids was determined, a total of 1.095 grams of acid (calculated as ricinoleic acid) being produced from 6 cc. of castor oil. From the results obtained with a similarly prepared extract of the germinated pumpkin seed, Lumia was not prepared to say whether the extract was capable of hydrolyzing oils or not, the increase in the fatty acids, even after seven days, being too trifling to warrant the conclusion that lipase was present. A few experiments were also made by Lumia with the resting seed of the cocoanut palm (*Cocos nucifera*) but only a very slight lipolytic effect was noted.

It is to Connstein, Hoyer and Wartenberg[2] that we owe most of our present knowledge of vegetable lipase and its activities. Their attention was confined to the resting castor-oil bean on which both Green and Sigmund had worked, and they found that under certain conditions, which they studied in detail, the zymogen in the resting seed could be converted into the active enzyme, and that, if sufficient time be given to the lipase in which to exercise its lipolytic action, the intensity of the hydrolysis is most marked, in some cases upward of 90 per cent. of the oil which had been worked into an emulsion with the seed being converted into free acid and glycerol. Among the many important results which were the outcome of this research, are two that deserve especial mention: first, that just as intense hydrolysis may be obtained with the resting seed as with the germinated; second, that Green's statement that free acid

[1] *Staz. sperim. agrar. ital.*, **31**, 397 (1898).
[2] *Ber.*, **35**, 3988 (1902).

hindered the hydrolysis is incorrect, but, on the contrary, it is necessary in order to obtain maximum hydrolysis.

Lipase has also been found in the jequirity seed (*Abrus precatorius*) by Braun and Behrend[1] but the conditions under which they worked were such that the seed showed no marked hydrolytic power.

Hoyer,[2] continuing the work of Connstein, Hoyer and Wartenberg, found it impossible to prepare a solution having notable hydrolytic power, from the resting castor-oil bean. Various attempts were made to isolate or concentrate the enzyme by mechanical means, but in this, Hoyer was likewise unsuccessful.

Fokin[3] has studied seeds of Russian origin to determine whether any of them had notable fat-splitting properties like the castor-oil bean. His examination included more than sixty different seeds from thirty different families, and he found but two that produced intense hydrolytic action. The seeds in question are the celandine (*Chelidonium majus*) and toadflax (*Linaria vulgaris*). Quite a number of seeds showed slight hydrolytic power (no experimental details are given with respect to these seeds), but none except these two were marked. Fokin's method of operation was akin to that of Connstein, Hoyer and Wartenberg.

Fokin has also made an extended study of the question of the decomposition of fats by enzymes[4] restricting himself, however, to a study of the lipase of the castor-oil bean. He has considerably extended our knowledge of the lipase of this bean and of the conditions under which it may operate to best advantage. It is to be noted that Fokin, like Hoyer, was unable to obtain a solution of the lipase which had any notable lipolytic power, such as is possessed by the bean itself.

Where Hoyer failed in working out a method of concentrating the enzyme in the castor-oil bean by mechanical means, Nicloux[5] has succeeded. Nicloux has shown how the cytoplasm of beans may be readily isolated mechanically, and proves that the hydrolytic power lies in the cytoplasm alone.

Walker and Bourne[6] also failed in an attempt to separate the lipase from the castor-oil bean and obtain a concentrated solution of

[1] *Ber.*, **36**, 1142, 1900 (1903).
[2] *Ibid.*, **37**, 1436 (1904).
[3] *Chem. Rev. u. Fett. u. Harz. Ind.*, **11**, 30, 48, 69 (1904).
[4] *Ibid.*, **11**, 91, 118, 139, 167, 193, 224, 244.
[5] *Compt. Rend.*, **138**, 1112, 1288, 1352 (1904); **139**, 143 (1904).
[6] *Tech. Quart.*, **17**, 284 (1904).

it. They found that germination lessens the intensity of the hydrolytic power of the bean.

Urbain, Saugon and Feige,[1] in a report of some experiments on the saponification of copra by means of the cytoplasm of the castor-oil bean, have brought out one point of especial interest, namely, that contrary to the statement of Connstein, Hoyer and Wartenberg they find that all glycerides are saponified with equal facility by the lipase of this bean. C., H., and W. found that the intensity of the hydrolysis of glycerides of fatty acids of low molecular weight was less than of those of high molecular weight, hence they assumed that all glycerides were not hydrolyzed with equal ease. The reason for this does not lie in the fact that the glycerides of fatty acids of low molecular weight are less easily saponified, but that one of the products of the hydrolysis, namely, the acid, as soon as it reaches a certain concentration, inhibits or destroys the activity of the lipase. This point is brought out very clearly with butyric acid, the authors showing that when the emulsion contains 10 per cent. of this acid, the hydrolysis is altogether stopped.

It is now generally assumed that during the germination of oleaginous seeds, a lipolytic enzyme is formed which hydrolyzes the oil present as a preliminary step in the utilization of this reserve food-stuff for the nourishment of the growing embryo. While this assumption may be correct, yet it rests on altogether too slender experimental grounds to warrant its acceptance as a principle applicable to all oleaginous seeds. The work of Green, Sigmund Lumia, Connstein, Hoyer and Wartenberg, as well as of Walker and Bourne, relates to but five germinated seeds. Of one of these five, namely, the castor-oil bean, C., H., and W. state that the germinated seed is no more active than the resting seed, while Walker and Bourne say that germination lessens its activity. However this may be, it is apparent that in the case of this bean, germination is unnecessary to demonstrate the presence of lipase and that it is capable of producing intense hydrolysis. With the germinated pumpkin seed, Lumia obtained entirely negative results. There remain then but the three seeds, on which Sigmund experimented, which may be used as a basis for the acceptance of the principle that lipase is produced during germination. It was necessary for Sigmund to show that under the same set of conditions the non-

[1] *Bull. Soc. Chim.* (3), **31**, 1194 (1904).

germinated seeds were less active; this he has done and the point appears to be proven.

Yet, since our knowledge of the lipase of the castor-oil bean has been so much extended, and we know the conditions most favorable for its activities, it is desirable to try other resting and germinated seeds under conditions which we now know are favorable for lipase to exercise its specific functions. Then if we obtain marked divergence in the intensity factor of the hydrolysis, it points still more clearly to the formation of lipase during germination. It has long been known that during germination, oleaginous seeds increase markedly in their acid content. If lipase is produced during germination, it then becomes evident what the function of this lipase is.

In the experimental part of this paper, we have studied four seeds in a resting state and two of them in a germinated condition. The resting flax, peanut, croton and almond seeds are not hydrolytic, or only so to a very slight extent. Neither is the zymogen of these seeds converted into an active enzyme by means which activate the castor-oil bean, celandine and toadflax. The experiments were carried over a sufficient period of time so that the time factor, so important in the case of the castor-oil bean, could be made use of, if such were possible. Failure to activate by these means, points conclusively to the fact that the zymogen of these seeds differs from those of the three seeds mentioned above.

Comparison of results obtained with the germinated flax and peanut, point unquestionably to the production of lipase during germination. A prolongation of the period over which the lipase could induce hydrolysis, showed that the hydrolysis augmented day by day, as would be expected, were lipase present. That hydrolysis was not due to bacterial action, was assured by the use of chloral, which Connstein, Hoyer and Wartenberg showed to be quite efficient for this kind of experimentation.

We have been able to prepare quite active solutions of lipase. In spite of numerous attempts, this has not been accomplished by those who have worked with the castor-oil bean. It is probable that not only the zymogen, but also the lipase of the bean differs from the lipase of the germinated flax and peanut.

The active solutions obtained from both the flax and peanut, produce a precipitate when treated with alcohol. The lipase, in the case of the peanut, is precipitated (doubtless along with much albuminoid matter), for the precipitate thus obtained shows marked

lipolytic power. Solutions of the flax lipase produce a precipitate when treated with alcohol, but this precipitate shows no hydrolytic activity. It is therefore evident that the lipase of the peanut differs from that of the flax.

Experimental Work.

RESTING SEEDS.

The following seeds were used in this part of the investigation: 1, peanut (*Arachis hypogaea*); 2, flax (*Linum usitatissimum*); 3, almond (*Prunus amygdalus*, var. *dulcis*); 4, croton (*Croton tiglium*).

At the outset of this investigation, it was necessary to determine what substance could be most expeditiously used in order to inhibit bacterial growth in the emulsions. A number of trials were made with toluene, but this was found useless for this type of work, although seemingly satisfactory in Buchner's zymase investigations[1]. Chloroform and chloral were investigated, and while the former was satisfactory in the majority of trials made, yet in a few, the emulsions were not prevented from souring. Chloral proved satisfactory in all cases and it was consequently adopted. We owe to Connstein, Hoyer and Wartenberg's work the suggestion as to the use of chloral.

The general method of procedure was as follows: The resting seeds were thoroughly ground until a mass of more or less buttery consistency was obtained.[2] This mass was then thoroughly mixed with olive oil; water (or dilute acid of known strength) added until a perfect emulsion was obtained, the whole emulsion being made as thoroughly homogeneous as possible. The chloral was incorporated with the water before addition. The exact amount of each ingredient was determined as added. In a few of the experiments, the ground seed was extracted with ether before use.

The resulting emulsion was then divided among a number of Erlenmeyer flasks (50 cc.), the weights of which had previously been accurately determined. By reweighing the flasks and their contents, we could then readily calculate the amount of the various constituents. These flasks were stoppered and placed in an incubator and kept at a constant temperature of 30°. The acid value of one of the samples was always determined at once, the others at varying intervals of twenty-four to forty-eight hours, in order to determine the progress of the hydrolysis.

[1] "Die Zymasegärung," p. 176.

[2] In all these cases, the seeds (except the flaxseed) were freed from their outer shell before using.

EXPERIMENT 1.

3.8 grams of the peanut butter, previously extracted with ether; 37.4 grams of oil; 10.2 grams of water; 0.4 gram chloral.

At once.	One day.	Two days.	Four days.	Six days.
3.5	5.5	3.7	3.9	4.5[1]

This shows very clearly that no hydrolytic enzyme exists as such in the resting peanut. The retrogression in the acid value following, in this case, the first day, has been noted in a number of cases. We are as yet unable to explain this retrogression. One explanation is possible, but we hardly think probable, namely, that our emulsions were not homogeneous. Great care was used in all cases to obtain perfectly homogeneous emulsions by prolonged trituration. Experiments 3 and 4, for example, give some idea of how the acid value increased very slowly from one determination to another without any retrogression or, in fact, any very *marked* increase, yet what increase there was, was fairly regular, pointing to the fact that the emulsions were homogeneous.

EXPERIMENT 2.

4.1 grams of peanut (same as in Expt. 1); 32.5 grams of oil; 12.1 grams of 0.4 per cent. sulphuric acid;[2] 0.35 gram chloral.

At once.	One day.	Three days.	Four days.	Five days.	Seven days.
4.1	5.6	4.8	6.2	7.3	7.5

The presence of mineral acid has not the power of activating the zymogen of the resting peanut. The most that can be said is that in the presence of mineral acids, the hydrolysis is but feeble.

This same experiment was repeated with peanuts that had not been extracted with ether, and, in the presence of small amounts of mineral acids, the results were of the same order as those just given, showing that the inactivity did not lie in any cause produced by the ether extraction.

EXPERIMENT 3.

7.5 grams of flaxseed; 32.4 grams of oil; 15 grams of water; 20.0 grams of 0.4 per cent. sulphuric acid; 0.35 gram of chloral.

At once.	One day.	Three days.	Five days.	Seven days.
2.9	4.3	7.1	8.0	9.8

[1] The acid value in all cases, unless otherwise stated, is based on the per cent. of oil in the sample, and represents the number of milligrams of potassium hydroxide necessary to neutralize the acids in 1 gram of the oil. All due corrections were made when mineral acids were present.

[2] Slightly weaker than $N/_{10}$ H_2SO_4. Connstein, Hoyer and Wartenberg found that the most intense action was produced by acid varying between $N/_{10}$ and $N/_5$.

As in the case of the peanut (Expt. 2) the flaxseed shows only a slight hydrolytic power. That even this slight hydrolytic power is not in any way due to the presence of the mineral acid, is shown by the following experiment, in which the addition of the mineral acid was omitted.

EXPERIMENT 4.

6.5 grams of flaxseed; 26.7 grams of oil; 31.4 grams of water; 0.36 gram of chloral.

At once.	One day.	Two days.	Four days.	Six days.
4.0	6.3	6.3	8.2	9.0

The higher acid value shown on immediate titration, is due to the fact that it was a different sample of oil from that used in the preceding experiment. As in Expt. 3, the results show that the flaxseed has a slight hydrolytic power, but by no means pronounced. Another experiment in which the total amount of mineral acid (calculated in per cent. of the emulsion) was only one-third that of Expt. 3, showed results comparable with that of Expts. 3 and 4.

EXPERIMENT 5.

7.8 grams of croton seeds; 40.8 grams of oil; 15.0 grams of 0.4 per cent. sulphuric acid; 0.43 gram of chloral.

At once.	One day.	Three days.	Five days.	Seven days.
7.1	8.3	9.8	10.6	11.2

EXPERIMENT 6.

9.5 grams of almonds; 28.2 grams of oil; 19.5 grams of 0.4 per cent. sulphuric acid; 0.42 gram of chloral.

At once.	Two days.	Four days.	Five days.
6.3	6.4	7.3	10.0

Experiments 5 and 6 show that the croton and almond seeds, like those of the peanut and flax, contain a zymogen which is but slightly, if at all, activated by mineral acids.

GERMINATED SEEDS.

The peanut and flaxseed were the only seeds used in these experiments. In germinating the peanut, they were first soaked in water for twenty-four hours and then planted in white pine sawdust which was kept moist. After germination for about a week at 30°, the hypocotyledonary portion was separated and rejected. The remainder of the seed was freed from external moisture, thoroughly

pulped, and in this condition used as in the experiments with the non-germinated seeds[1].

Of a large number of experiments carried out with the germinated peanut, only two need be given.

EXPERIMENT 7.

19.4 grams of germinated peanut; 33.1 grams of oil; 8.9 grams of 0.4 per cent. sulphuric acid; 0.35 gram of chloral.

At once.	One day.	Three days.	Four days.	Six days.
6.4	10.5	13.0	14.8	29.3

This experiment shows very clearly the formation of lipase during germination. The hydrolysis steadily increased up to the fourth day, and during the next forty-eight hours, the acid value increased to about twice the value obtained on the fourth day. This marked increase is akin to the "Sprung" of Connstein, Hoyer and Wartenberg, but in degree, is not so intense.

EXPERIMENT 8.

Another sample of germinated peanut, gave the following results.

9.4 grams of germinated peanut; 30.6 grams of oil; 10.0 grams of 0.1 per cent. sulphuric acid; 0.31 gram of chloral.

At once.	One day.	Two days.	Four days.	Six days.
4.9	8.9	11.3	17.0	34.8

These results are quite similar to those of Expt. 7, except that the total amount of mineral acid was considerably reduced, without any marked effect on the general trend of the results. In this experiment, the total amount of germinated peanut used was (based on its per cent. of the emulsion) a little over half that of the previous experiment.

When we compare the results of the last two experiments with those obtained with the resting peanut, it at once becomes evident that lipase is produced during the process of germination.

A few experiments were made to concentrate the lipase of the germinated peanut. The germinated seeds were very thoroughly ground with clean quartz sand and a very small amount of water.

[1] In calculating the acid value, based on the oil in the sample, the results are necessarily slightly in error due to the free fatty acids developed during germination. This error is, however, constant throughout any experiment. The same is true of the results in Experiments 3, 4, 5 and 6, due to small amounts of free fatty acids in the non-germinated seeds.

This grinding with sand was done to break up the cells of the germinated seed. The resulting mass was then subjected to a pressure of about 250 atmospheres, the press liquor obtained being of a grayish color and slightly turbid. This press liquor was poured into absolute alcohol and the precipitate thus obtained was filtered, washed thoroughly with ether and then dried *in vacuo*. The final product was grayish in color but became somewhat darker on standing.[1]

The following experiments show that the lipase had been extracted from the germinated seed and that the precipitated product was very active.

EXPERIMENT 9.

3.0 grams of the precipitate; 30.7 grams of oil; 12.3 grams of water; 0.41 gram of chloral.

At once.	Two days.	Three days.	Five days.	Seven days.
8.9	30.9	37.4	45.7	53.2

EXPERIMENT 10.

2.7 grams of precipitate; 32.5 grams of oil; 10.0 grams of 0.4 per cent. sulphuric acid; 0.41 gram of chloral.

At once.	One day.	Two days.	Four days.	Six days.
7.1	25.2	39.4	50.9	60.3

In Expts. 9 and 10, the precipitated product used formed respectively but 6.5 and 5.9 per cent. of the total emulsion; *i. e.*, the hydrolysis was brought about by a comparatively small amount of the precipitated product, showing clearly that the lipase had been concentrated.

A number of experiments were also carried out with the press liquor itself, but it is unnecessary to give the figures obtained. We found that gum acacia was necessary in these experiments to obtain a permanent emulsion. All the experiments with the press liquor showed that this liquor contained lipase, and that it was quite active in hydrolyzing oils.

Germinated Flaxseed.—The germinated flaxseed used in these experiments, was prepared as follows: The seed was placed between layers of moist filter-paper and kept at 30°, the papers being moistened from time to time. In twenty-four to forty-eight hours, the seed had germinated, in some cases, the hypocotyledonary portion being nearly a centimeter long. These seeds were then thoroughly macerated and the resulting paste used as in the preceding experi-

[1] This method is similar to the method employed by E. Buchner in extracting zymase from the yeast cell.

ments. While a large number of experiments under varying conditions and with varying amounts were carried out, yet it will be unnecessary to give more than one experiment in order to show that, as in the case of the peanut, lipase is produced during the germination of the flaxseed.

EXPERIMENT II.

14.2 grams of germinated flaxseed; 23.3 grams of oil; 18.8 grams of water; 8.0 grams of 0.4 per cent. sulphuric acid; 0.36 gram of chloral.

At once.	One day.	Two days.	Four days.	Seven days.
6.7	24.5	34.7	52.5	74.4

If germinated flaxseed is ground with sand in order to disrupt the cells, and then treated with a small amount of 5 per cent. salt solution, the resulting mass being afterwards subjected to 250 atmospheres pressure, a press liquor is obtained which is grayish in color, turbid and viscous. When this liquor is used to induce hydrolysis, gum acacia is necessary in order to obtain a permanent emulsion. As was expected, this liquor was found capable of hydrolyzing oils.

A number of attempts were made to precipitate the lipase from this press liquor after the fashion used in precipitating the peanut press liquor. A bulky, stringy, slightly grayish precipitate was always obtained, which, on standing, became much darker in color. We found that when prepared in this way, the precipitate showed practically no hydrolytic power, the press liquor from which it had been obtained having been, however, active. In the production of an emulsion with this product, a large amount of water seemed to be necessary.

It was found impossible in this case to determine whether the lipase in the press liquor from the germinated flaxseed was water-soluble or not, for the press liquor was always so viscous as to render it impossible of filtration even after dilution, so that no satisfactory aqueous solution quite free from turbidity could be obtained to work with.

It is certain, however, that the active lipase in the turbid and viscous press liquor, if precipitated by the alcohol, is in such a form as to be no longer capable of inducing hydrolysis. In preparing the press liquor, varying methods were used; for example, in one case, the germinated seed was ground alone with sand and then pressed; in another, small amounts of water were used in addi-

tion to the sand; again, water, sand and Fuller's earth—but all of these gave inactive precipitates. Only one experiment need be given to show the type of results obtained.

EXPERIMENT 12.

7.0 grams of precipitate; 33.9 grams of oil; 29.9 grams of 0.4 per cent. sulphuric acid; 0.35 gram of chloral.

At once.	One day.	Three days.	Five days.	Seven days.
0.8	1.4	2.7	3.9	3.1

In conclusion, we wish to return to the question of the retrogression in the acid value, several examples of which occur in the experiments cited in this paper. We have met with this phenomenon a number of times, and the following experiment, which we have selected especially for this purpose, shows this admirably.

EXPERIMENT 13.

	At once.	Two days.	Four days.	Five days.	Six days.	Seven days.
Mineral acid present in terms of N H_2SO_4	0.41	0.33	0.37	0.38	0.48	0.38
Fatty acid in the oil in terms of N acid	0.21	0.17	0.19	0.19	0.24	0.19
Total acid	0.62	0.50	0.56	0.57	0.72	0.57
N KOH to neutralize the sample	0.45	0.49	0.45	0.49	0.69	1.38

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MECONIC ACID IN THE U. S. P. 1890 ASSAY OF OPIUM AND CERTAIN MECONATES.

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THE work outlined in the following pages has to do with the identification and properties of an impurity which usually contaminates, to a greater or less degree, the precipitated morphine which is obtained as the "form" to be weighed in the present (1890) U. S. P. method for the assay of opium. Incidentally, some of the salts of meconic acid with barium and calcium were prepared and examined. It should be stated at the outset that these salts seem to have a somewhat variable composition and offer

considerable difficulty in their analysis. They are insoluble in all ordinary solvents and could not be purified by crystallization. The agreement between the theory and our analyses is therefore not very close.

The U. S. P. 1890 assay process consists in a thorough extraction of the opium with water and precipitation of the morphine as alkaloid by addition of dilute ammonia water to the concentrated aqueous extract. A certain amount of alcohol and ether are added to the flask containing the concentrated aqueous extract before the ammonia; this yields a purer morphine. The formation of a thin layer of a white or yellowish-white substance adhering to the bottom of the flask containing the precipitated morphine was observed with many varieties of opium, notably the "Yerli" and "Boghaditch" from Smyrna. The precipitated morphine, on the other hand, does not adhere to the flask and by using alcohol saturated with morphine it may oftentimes be washed out of the flask (a small Erlenmeyer), leaving the coating of the yellowish-white substance on the bottom. If water is used instead of alcohol saturated with morphine, the yellowish-white substance is loosened, being partially soluble. If the contents of the assay flask are transferred to the filters in the regular manner by means of a rubber-tipped rod, the yellowish-white body appears in small flakes or scales scattered through the crystalline precipitate of morphine and is weighed as such. It is generally known that the precipitated morphine produced by the U. S. P. 1890 assay is not of sufficient purity to weigh as morphine and many methods of determining the amount of impurity have been proposed. In order to obtain a purer precipitate of morphine Lamar[1] devised a modification of the U. S. P. 1890 process in which alcohol was added to the concentrated aqueous extract of the opium just before the precipitation of the morphine. The alcohol produces a precipitate, containing no morphine, which can be filtered off and the filtrate is evaporated again and the morphine precipitated as usual with dilute ammonia. This process has been used in our laboratory and the resulting morphine is nearly, if not quite, free from scales of the white body. We thought that the precipitate produced by alcohol in the Lamar modification was probably identical with the yellowish-white substance which we had observed in the precipitated morphine obtained in the regular process, but investigation proved this not to be the

[1] Lamar: *Am. J. Pharm.*, **72**, 36 (1900).

case. The precipitate produced by alcohol was found to be chiefly calcium sulphate and some gummy substances of dark color.

The yellowish-white coating is not calcium sulphate; some scales of it were washed free of morphine on a copper sieve and tests showed calcium and meconic acid present. As it was customary to determine the purity of the weighed morphine by titration with N/10 H_2SO_4, it became important to ascertain whether the white body influenced the titre. Experiments with small amounts showed that it consumed nearly one-fourth as much acid as the same weight of morphine. Its acid-consuming power was also indicated by the fact that titrations of assay morphine containing much of the yellowish-white substance (which we shall call simply "scale" hereafter) were far too high, as was proved by subjecting the morphine to another assay, thus determining its true purity. The following figures show the magnitude of the error:

	Average purity by titration Per cent.	Average purity by re-assay. Per cent.
Assay morphine from 14 assays of Salonica opium *poor in "scale"*	96.5	94.5
Assay morphine from 3 assays of Smyrna opium *rich in "scale"*	95.1	87.9

We thought that the "scale" was probably some basic salt of calcium and meconic acid, and accordingly attempted to reproduce it from pure material before making analyses of it. A solution of calcium nitrate was added to a solution of meconic acid made noticeably alkaline with ammonia. A voluminous, yellowish-white precipitate formed at once which settled very slowly, and owing to its gelatinous nature filtered with difficulty and dried into a lemon-yellow horn-like substance apparently without crystalline structure. It was observed that the mother-liquor no longer smelled of ammonia although previous to the addition of calcium nitrate the excess of ammonia was quite evident, and in fact the mother-liquor under these conditions was actually acid, as we found later. The lemon-yellow salt, after washing and drying at 60°, consumed only about 1.5 cc. of N/10 H_2SO_4 for 0.5 gram and after long digestion on the water-bath with 10 cc. N/10 H_2SO_4 about 2.0 cc. N/10 H_2SO_4 were consumed. Litmus paper was used as indicator. Ten cc. of N/10 H_2SO_4 digested on a water-bath similarly showed no appreciable loss of acid. The same amount of "scale" under like treatment would require about 4.0 cc. N/10 H_2SO_4. The lemon-yellow salt also lacks the physical properties of the "scale" and

we concluded that they were not identical, a conclusion which subsequent experience verified. The salt loses little or no water at 100°, but attains approximate constancy at 150-160° C., the loss of weight amounting to 24.5 per cent. Calculated for $Ca_3(C_7HO_7)_2.9H_2O$, 23.9 per cent.

The determination of lime in the dried salt gave 28.5 and 28.7 per cent. of calcium oxide; calculated, 32.17 per cent. A correct determination of lime in a meconate by incineration was found to be very difficult, if not impossible. The salt ignites and burns like moist gunpowder, no matter how gradually the heat is increased. It was found best to keep the crucible tightly closed until organic matter is nearly all consumed.

The dried salt was slightly discolored superficially. The air-dried salt before drying at 160° gave a strong test for ammonia with lime. No means of dissolving and crystallizing this salt was found. It was found later that tribarium meconate gives off small amounts of carbon dioxide when similarly heated, and an ammonium calcium meconate is also described later which gives off large amounts of ammonia and carbon dioxide. The low content of calcium, the great loss in drying, and presence of ammonia show that the yellow salt is not a pure tribasic calcium salt, but contaminated with ammonium calcium meconate.

Assay Scale.—The conditions under which "scale" is formed in the assay flasks are abundance of meconic acid and of ammonia and scarcity of calcium, for the amount of the latter naturally occurring in opium is small in comparison to the meconic acid. After several different methods had failed to yield a product anything like the assay "scale," the following procedure was successful. Four grams of crystallized meconic acid were dissolved in 100 cc. of water containing a little alcohol. This solution in a flask was now covered with a layer of ether, and ammonia water added in excess followed by 25 cc. of a solution of calcium nitrate which analyzed 1.674 grams CaO per 100 cc. At first the same yellow voluminous precipitate formed as was previously obtained in adding calcium nitrate to meconic acid saturated with ammonia, but it re-dissolved on shaking and after a few minutes a white flaky salt began to form and precipitate slowly on the bottom of the flask. About 2.2 grams of the salt were obtained which had the physical appearance of the "scale" from assays, except that it was white instead of yellowish-white.

If a concentration greater than the above proportions is used or if the solution is warmed, the lemon-yellow tribasic calcium salt will not all dissolve.

Determinations of the lime content in this salt (which we shall call "artificial scale" to distinguish it from the "assay scale" obtained from actual assays on opium) and in "assay scale" were made by incinerating and weighing the calcium oxide produced. It was found that both the "artificial scale" and the "natural scale," after thorough washing, gave strong tests for ammonia with lime. Kjeldahl determinations for ammonia were therefore made.

The recrystallized assay scale was prepared by dissolving assay scale in cold dilute hydrochloric acid and reprecipitating with ammonia. It is slightly soluble in water but no solvents were found from which to crystallize it. Under the microscope, this salt and the "artificial scale" showed the same form of crystals (diamond-shaped plates, often cut off at the four points). The "natural scale" viewed under the microscope appeared as such a closely interlaced mass that its crystalline structure could not be made out. The presence of the coloring-matter in the form of a gum is probably responsible for this fact.

No accurate determinations of the crystal water in the "artificial" and "assay scales" were possible by heating. On drying at various temperatures up to 160° no constancy of weight was reached but both salts lost about equally, the losses being as high as 30 per cent. of the air-dried weight. After drying for about a week, day and night at 160° both salts were still losing weight, but it was observed that now the salts gave very weak tests for ammonia with lime, whereas at the start the air-dried salts gave strong tests. Experiment showed that both carbon dioxide and ammonia were given off. It is well known that meconic acid loses carbon dioxide easily when heated in the dry state or when boiled with water or with water containing acid, forming comenic acid by the loss of one of the two carboxyl groups[1]. Under certain conditions a second molecule of carbon dioxide may be lost and pyrocomenic acid forms. How[2] has shown that a solution of meconic acid saturated with excess of ammonia upon prolonged boiling yields, when acidified, carbon dioxide and a precipitate which upon drying turns out to be comenic acid amide, $C_5H_3O_3CONH_2$. In view of these facts, we thought that if the calcium ammonium meconate were heated

[1] *Ann. Chem.*, **7**, 237 (1833).

[2] Henry How: *Ann. Chem.*, **83**, 350.

under proper conditions for measuring the ammonia and carbon dioxide evolved, the reaction might be shown to run as follows:

$$CaNH_4C_7HO_7 \text{ (``scale'')} = NH_3 + CO_2 + CaC_6H_2O_5 \text{ (calcium comenate).}$$

Accordingly, a slow current of air free from carbon dioxide and ammonia was passed over artificial scale heated to 160° and thence through flasks containing determinate amounts of dilute sulphuric acid and barium hydroxide. After drying for different times, samples from the absorption tube were withdrawn and the amounts of ammonia and carbon dioxide given off determined by titration; the results are as follows:

0.25 GRAM "ARTIFICIAL SCALE."

	Time of heating in days of twenty-four hours.			
	Six days. Gram.	Eleven days. Gram.	Fifteen days. Gram.	Theory for $CaNH_4C_7HO_7$. Gram.
NH_3 produced.....	0.01054	0.01135	0.01135	0.01380
CO_2 produced	0.02517	0.03795	0.04697	0.03558

The above experiment was made only once and the results need confirmation. It seems evident that the reaction does not run easily and that decomposition goes farther than the production of calcium comenate.

One attempt to determine the crystal water was made by heating the salt in such a manner that the ammonia and water were absorbed in sulphuric acid. From the gain in weight of the sulphuric acid tube we deducted the weight of ammonia that would have been given off according to the above equation and considered the resulting gain as due to crystal water. This method should give results approximately correct since the greater part of the ammonia is given off on prolonged heating. A test-tube containing 0.500 gram of artificial scale was placed horizontally in a drying oven and a delivery tube led out and joined to a U-tube filled with sulphuric acid and standing in cold water. The absorption of moisture from the air was prevented by a long capillary tube open at one end, sealed on to the U-tube at the other end. After several days' and nights' heating at 160-170° C., the acid gained weight—0.105 gram. If the salt has the formula $CaNH_4C_7HO_7.3H_2O$, 0.500 gram would yield 0.0276 gram NH_3; hence, the water given off = 0.105 — 0.0276 = 0.0774 gram.

All the analyses of the salt are grouped below:

	Calculated for $CaNH_4C_7HO_7.3H_2O$. Per cent.	Found. "Artificial scale." Per cent.	Found. "Assay scale." Per cent.	Found. "Assay scale" recrystallized. Per cent.
CaO	18.16	18.24	.....	17.18
NH_3	5.52	5.53	5.28	5.32
H_2O	17.47	15.5	.....	.....

From the results of the analyses and mode of preparation of the salt, we conclude that the unknown yellowish-white "scale," which occurs in the morphine from U. S. P. assays on certain opiums, is a double salt of calcium and ammonium with meconic acid represented by the formula $CaNH_4C_7HO_7.3(?)H_2O$. The content of water we do not feel certain of. This salt or some similar double salt was known to Robiquet.[1] He states that upon treating an aqueous extract of opium with ammonia, there is precipitated along with the morphine a part of the meconic acid in the form of an insoluble double salt of lime and ammonium. After the extraction of the morphine alkaloid from the precipitate caused by the ammonia there remains this "dreifach mekonsaures Salz." The presence of alcohol and ether is the only point of difference between Robiquet's experiment and the present U. S. P. 1890 assay of opium, and these additions would, in fact, tend to produce a more complete separation of calcium ammonium meconate with the morphine, so it appears that as early as 1833 this difficulty in the precipitation of a pure morphine from an aqueous extract was known, and yet it seems to have been largely overlooked in the 1890 assay. Robiquet did not analyze his salt, and we have been unable to find any other reference to the existence of the compound.

Meconic Acid and Bases.—In the first preparation of the lemon-yellow tribasic calcium meconate, it was mentioned that the mother-liquor became acid. Liebig[2] observed the same phenomenon when silver nitrate is added to meconic acid neutralized with ammonia and recognized that the cause was the varying basicity of meconic acid towards different bases. He prepared an insoluble yellow silver salt having the formula $Ag_3C_7HO_7$ and mentions that the so-called "neutral potassium meconate" is a dibasic salt of the formula $K_2HC_7HO_7$. Stenhouse[3] found that meconic acid forms a salt with lead in which three hydrogen atoms were replaced by the metal. The generally accepted formula for

[1] *Ann. Chem.*, **5**, 82; see also Gmelin-Kraut, "Handbuch Org. Chem.," Vol. III, p. 338 (1859).

[2] *Ibid.*, **26**, 114 (1838).

[3] *Ibid.*, **51**, 231 (1844).

meconic acid is $C_5HO_2\begin{cases}OH\\COOH\\COOH\end{cases}$ in which the hydrogen of the hydroxyl group most probably forms the third acid hydrogen toward the above-mentioned metals. That the acid behaves quite accurately as a tribasic acid also toward calcium and barium is shown later by the preparation of the tribasic salts.

A preliminary titration was made to test this point. To a solution of 0.2 gram of crystallized meconic acid we added 4.17 cc. of a certain solution of calcium nitrate. To produce $Ca_3(C_7HO_7)_2$ would have required 3.94 cc. of the same solution. Decinormal sodium hydroxide solution was now run in until the mother-liquor over the precipitated salt was just alkaline to litmus; this required 23.8 cc. It was found that the calcium nitrate solution was slightly acid, 4.0 cc. requiring 0.10 cc. N/10 NaOH; hence, deducting this from 23.8 cc., we have the acidity developed in reaction 23.7 cc. N/10 acid. For the reaction $2H_3C_7HO_7+3Ca(NO_3)_2+6NaOH=Ca_3(C_7HO_7)_2+6NaNO_3+6H_2O$, the sodium hydroxide required for 0.2 gram acid is 23.62 cc. The agreement is close. On the other hand, meconic acid, if pure and free from comenic acid, titrates accurately as a dibasic acid with sodium hydroxide, using litmus paper as indicator. If the acid is sufficiently white, so that its solution is colorless, it furnishes its own indicator, so to speak, for as soon as more than two equivalents of alkali are added a very perceptible yellow color appears. This change is delicate enough to detect an excess of two or three drops of N/10 alkali. If comenic acid is present, as much as 10 or 15 cc. N/10 alkali in excess must often be added in an ordinary titration to effect a definite end-point as indicated by red litmus paper.

BARIUM AND CALCIUM SALTS OF MECONIC ACID.

In order to gain some knowledge of the behavior of meconic acid in the presence of varying amounts of calcium we attempted to replace successively one, two or three of the acid hydrogen atoms with equivalents of calcium. Barium salts were also made on account of the greater ease of handling the base quantitatively. Some of these salts have been prepared before, but the literature on the subject is not very complete. Beilstein, for example, does not give formulas of, or references to, the calcium or barium salts of meconic acid. Fehling's "Handwörterbuch," 1871 (Vol. IV, p. 294), gives formulas for the dibasic meconates of barium and calcium and

for the acid calcium salt, but nothing in regard to the tribasic salts of barium and calcium. Similarly "Watts' Dictionary" (1901 edition) gives no information on these tribasic salts. Probably the best description of the early work upon the preparation of meconic acid and its salts, with many references to the original articles, is to be found in Gmelin-Kraut's "Handbuch der Organ. Chem." Vol. III, p. 332, etc. (1859). His statements must be accepted with discrimination, however, for it must be remembered that much of the early work on "meconic acid" is quite invalid because of the mode of preparation which yielded not meconic acid at all, but an impure pyromeconic acid. Although this is pointed out, it is not made clear in each description of a salt of meconic acid whether the acid was pure and properly prepared and furthermore, in some cases, the properties indicate an impure pyromeconate rather than a meconate. For example, on p. 338 under barium meconate, the statement is made on Robiquet's authority that the "pure meconic acid" does not precipitate a solution of barium hydroxide and immediately following comes a direct contradiction of this on Wackenroder's authority, to the effect that the acid gives with excess of barium hydroxide solution a slimy, heavy, yellow precipitate. The probable explanation is that the extract from Robiquet was based on work done before he knew that this acid, which was prepared by sublimation, was really an impure pyromeconic acid and not meconic acid at all. Wackenroeder[1], working about eight years after Liebig[2] had shown the true relationship of meconic, comenic and pyromeconic acids, obtained the correct reactions.

Again on p. 338 a formula is given for barium meconate which, after transforming to modern equivalents, becomes $BaHC_7HO_7.H_2O$ and the salt is described as being difficultly soluble in water but readily soluble in a solution of barium hydroxide with the production of a yellow color. Liebig is the authority for this, but we have looked up all the references to original articles by Liebig given by Gmelin-Kraut without finding any such statement. Fehling's "Handwörterbuch" gives the same information, but does not attribute it specifically to Liebig.

We have repeated Wackenroeder's experiment and find, as he did, that pure meconic acid, even with a large excess of barium hydroxide, produces a yellow flocculent precipitate which does not redissolve and cannot be made to do so by shaking or warming. We have

[1] *Archiv. für Pharm.*, **2**, 167 (1841).
[2] *Ann. Chem.*, **7**, 237 (1833).

tried this repeatedly with small amounts of acid and large amounts of barium hydroxide and always with the same result. Comenic acid, while giving a precipitate with barium hydroxide solution of greater solubility in the excess than the corresponding one produced by meconic acid, is still far from what we would call soluble in the excess. The precipitate so produced by meconic acid, as will appear later, is the tribarium salt. If Liebig made the statement above attributed to him, it is probable that it was taken from some early experiments prior to 1833 and hence with meconic acid that was open to objection on the grounds of improper preparation.

The meconic acid used throughout this work was prepared essentially after the method of Gregory[1] which consists simply in precipitating an aqueous extract of opium with calcium chloride and treating the resulting precipitate of crude calcium meconate with sufficient hydrochloric acid, somewhat diluted, to take it nearly into solution while hot. The clear filtered solution separates out crystals of meconic acid upon cooling which may contain some calcium. This can be separated by several crystallizations from warm water and a pure acid obtained. We were careful to avoid prolonged heating, as well as the use of very concentrated hydrochloric acid, both of which, as is well known, cause the acid to decompose. Our acid had a faint cast of yellow color, which is very difficult to remove, and had lost a little of its water of crystallization, otherwise we believe it quite pure. It gave no appreciable residue upon igniting it on platinum foil, which would indicate the absence of calcium. The last traces of calcium are difficult to remove, and two treatments with hydrochloric acid were required.

Attempts to Prepare Acid Barium Meconate.—This salt requires $Ba(OH)_2 + 2H_3C_7HO_7$. A solution of 24.79 grams of crystallized meconic acid (titrating 106.7 per cent. pure, owing to a loss of some of the crystal water) in about 600 cc. of warm water was added to 400 cc. of a solution of barium hydroxide which was $2.603 \times N/10$. A white crystalline precipitate formed after about one minute. After several hours, yellowish crystals of a different form made their appearance and settled out with the bulk of the precipitate. The precipitated salt, after washing with a little water and drying at 54°, weighed 21.8 grams.[2] The mother-liquor was intensely acid and, after standing, separated some of the same yellowish crystals which

[1] *Ann. Chem.*, **24**, 43.

[2] The barium actually carried down, according to the formula $BaHC_7HO_7 \cdot 3H_2O$, should yield 19.96 grams of salt.

were observed above. These crystals were found to be entirely soluble and nothing but pure meconic acid. A titration of a sample of the mother-liquor showed that if the acidity was figured as crystallized meconic acid, it would correspond to 11.07 grams for the whole of the mother-liquor or nearly one-half of the total meconic acid used. On the other hand, the barium in the mother-liquor, determined by weighing as barium sulphate, amounted to only 0.11 gram Ba; hence, the acid must have been present as uncombined acid. Moreover, some of the yellowish crystals, more or less contaminated with the white crystals which constituted the bulk of the precipitate, were picked out of the dried salt and were found to require 9.10 cc. N/10 alkali for neutralization, whereas the barium found corresponded to only 1.48 cc. N/10 $Ba(OH)_2$.

Under the microscope the yellowish and the white crystals were seen to have distinctly different forms[1], hence there is no doubt that meconic acid as such crystallized out with the salt proper and because of its sparing solubility in cold water was not removed by the washing. The salt was now subjected to thorough washing and upon analysis gave the following:

I. 0.500 gram dried at 54° gave 0.2873 gram $BaSO_4$.

II. 0.500 gram dried at 54° gave 0.2380 gram $BaCO_3$.

	Calculated for $BaHC_7HO_7.3H_2O$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
Ba	35.28	33.80	33.12

These values are very close to those obtained for the *neutral* barium meconate described below.

It seems evident that under the conditions of temperature and concentration here used, the salt forming from a mixture of barium hydroxide and meconic acid in proportion of one molecule of base to two molecules of acid is the dibarium meconate represented by the formula $BaHC_7HO_7$, and not a salt containing one equivalent of barium. From a preliminary experiment it seems probable that the acid salt is easily prepared when hydrochloric acid is present[2].

Neutral Calcium Meconate and Barium Meconate.—These salts require $Ca(OH)_2$ (or $Ba(OH)_2$) $+ H_3C_7HO_7$. A solution of 3.75 grams of crystallized meconic acid, which had been exactly neutralized with N/10 sodium hydroxide, was added to a solution of

[1] It was afterwards found possible to get yellowish crystals of the same form from a solution of pure meconic acid in water by sufficiently slow cooling.

[2] We made a similar experiment with calcium and meconic acid. These results we have rejected because of a neglected precaution which negatives their value.

calcium nitrate containing calcium equivalent to 0.837 gram CaO. A finely crystalline white salt formed after about one minute which, dried at about 60°, weighed 4.05 grams. Theory for $CaHC_7HO_7.2H_2O = 4.04$ grams for $3H_2O = 4.31$ grams. The amount of calcium remaining undissolved in the mother-liquor was not determined, hence no correction can be made for the dissolved salt, and this fact perhaps explains the low yield. The salt agitated with cold water gives a neutral reaction with litmus paper. If, however, the water is left in contact for a long time a slight acid reaction develops, and if the salt is boiled with water it becomes yellowish and a strong acid reaction develops in the water. Similarly, if the salt is warmed with excess of decinormal caustic soda it quickly becomes yellowish and the salt loses its crystalline appearance and is converted into a voluminous light yellow precipitate, which resembles the tricalcium meconate. The salt seems to be decomposed by the action of water with the formation of a more basic salt and liberation of acid. Peratoner and Tamburello[1] obtained a salt having the formula $CaHC_7HO_7.4H_2O$, as a *yellowish* crystalline precipitate by adding calcium chloride to a solution of meconic acid exactly neutralized with ammonia. Our salt, on the other hand, was white. We can see no explanation for this other than the possibility that the salt became somewhat basic through the subsequent action of water.

To prepare neutral barium meconate we brought together 400 cc. of a solution of barium hydroxide which, as before, was $2.603 \times N/10$ and a solution of 12.39 grams of crystallized meconic acid (titrating 106.7 per cent. pure, owing to loss of some of the crystal water). These proportions correspond to one molecule of barium to one molecule of crystallized meconic acid. The volume of the solution was diluted up to 1 liter. After about one minute a nearly white crystalline salt separated which, dried at 54° C., weighed 19.77 grams. The mother-liquor reacted faintly acid and contained 0.339 gram Ba as found by precipitating as barium sulphate. The barium actually carried down in the salt is, therefore, 7.153 grams (amount of Ba in 400 cc. $Ba(OH)_2$) — 0.339 = 6.814 grams Ba, and the theoretical yield for this amount of barium based on the formula $BaHC_7HO_7.3H_2O$ is 19.32 grams. One-half gram samples of the 54° dried salt gave for $BaCO_3$ on incineration: I, 0.2396 gram; II, 0.2383 gram; III, 0.2358 gram; IV, 0.2395 gram. Similarly, the one-half gram gave 0.2878 gram $BaSO_4$.

[1] *Chem. Centrbl.*, **1**, 45 (1904).

	Calculated for $BaHC_7HO_7.3H_2O$.	Found by weighing $BaCO_3$.				Found by weighing $BaSO_4$.
		I.	II.	III.	IV.	I.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Ba.....	35.28	33.34	33.16	32.82	33.34	33.86

It should be observed that the percentage of barium agrees well with that found in the washed salt of the previous preparation. In neither case, however, is the percentage of barium as high as the formula requires. The reason is not apparent; it may be that the salt contained hygroscopic moisture which the temperature of 54° failed to remove completely.

Peratoner and Tamburello obtained the salt corresponding to the formula $BaHC_7HO_7.3H_2O$ by precipitating meconic acid exactly neutralized with ammonia with barium chloride.

Neutral barium meconate behaves like the analogous calcium salt with water and sodium hydroxide, splitting off acid and coloring yellow with the formation of basic salt, but the change takes place more slowly than with the calcium salt.

Basic or Tricalcium Meconate and Basic or Tribarium Meconate.—These salts correspond to the proportion of $3Ca(OH)_2$ (or $3Ba(OH)_2$) to $2H_3C_7HO_7$. The calcium salt was prepared first from the lime and the acid and then from calcium nitrate, sodium hydroxide and the acid. Ignited calcium oxide, weighing 1.068 grams, was digested in a closed flask with a little over a liter of water and the clear solution filtered off from some undissolved oxide which, upon ignition, weighed 0.1044 gram. To the clear solution (containing $1.068 - 0.1044 = 0.9636$ gram CaO), we added a solution of 2.91 grams of crystallized meconic acid. At once, a gelatinous light yellow-colored precipitate of great volume formed. On standing, it settled easily but contracted immensely upon drying. The salt is apparently amorphous; under the microscope no crystals are to be seen and there is no effect on polarized light.

One-half gram of the air-dried salt, after drying five days at 60°, ceased to lose moisture and weighed 0.4626 gram. The temperature was raised to about 160° and after drying for three days the weight attained approximate constancy at 0.3816 gram. The salt was discolored yellowish, but only the surface, the inside remaining light yellow.

One-half gram of the air-dried salt upon incineration gave 0.1182 gram CaO.

The same salt was next made by adding a solution of 5.05

grams of crystallized meconic acid, to which three equivalents of sodium hydroxide had been added, to 100 cc. of a solution of calcium nitrate containing calcium equivalent to 1.674 grams CaO. The precipitate resembled the previous one in all respects and after drying at 60° weighed 6.4 grams. After the precipitation, the mother-liquor was slightly acid requiring 1.5 cc. N/10 NaOH[1] and contained calcium equivalent to only 0.1375 gram CaO. The salt, on the other hand, contained only a trace of sodium. It, therefore, cannot be a double salt of calcium and sodium, but must contain three equivalents of calcium.

One-half gram of the air-dried salt was dried at 60° until approximate constancy was attained; the weight was then 0.4802 gram. The same sample was now dried to constancy at about 160° when it weighed 0.3881 gram. Three determinations of the lime in this salt for 0.500-gram samples gave 0.1230 gram, 0.1219 gram, 0.1248 gram. The dried weight of 0.500 gram of the salt, as found above, was 0.3881 gram. The meconic acid was roughly determined in this salt by liberating it with oxalic acid and titrating. Allowance was made for the excess of oxalic acid present since the amount could be calculated from the acid used and the calcium present. The experiment was conducted as follows:

One-half gram of air-dried tricalcium meconate (containing by average of three determinations calcium equivalent to 0.1232 gram CaO) was triturated with 0.300 gram of crystallized oxalic acid and allowed to stand for several hours. The oxalic acid required for 0.1232 gram CaO is 0.2769 gram. The precipitate of calcium oxalate thus formed was free from meconic acid after washing, hence no meconate crystallized out with it, and it was thought that titration of the mixture, without removing the precipitate, would properly determine the meconic acid together with the excess of oxalic acid present. Two trials gave (1) 29.28 cc. and (2) 29.43 cc. N/10 NaOH.[2] The analyses on the two preparations are summarized below:

		Found.			
		Salt from base and acid.	Salt from $Ca(NO_3)_2+3NaOH$.		
	Calculated for $Ca_3(C_7HO_7)_2+6H_2O$.		I.	II.	III.
		Per cent.	Per cent.	Per cent.	Per cent.
Ca	19.33	18.27	18.31	18.15	18.58
H_2O	17.36	17.51	19.18	.....	.....
$H_3C_7HO_7$	64.27	.....	61.0	61.3	.....

[1] The calcium nitrate used was slightly acid, requiring for 100 cc. 2.4 cc. N/10 NaOH to neutralize it.

[2] These figures have been corrected for the sodium hydroxide used up by the excess of oxalic acid, 0.2769 gram.

It will be seen that the analyses fall a little short, in respect to calcium and meconic acid, of the formula $Ca_3(C_7HO_7)_2.6H_2O$. The agreement, however, between the theoretical ratio of calcium to meconic acid and the ratio found in the analyses is close, as may be seen from the following:

	Theory.	Found. (Salt from $Ca(NO_3)_2+3NaOH$.)
$\frac{3Ca}{2H_3C_7HO_7}$	0.3008	0.3001 average

Since the salt is a gelatinous, amorphous precipitate which we were unable to purify, owing to its general insolubility, it is doubtful whether any closer agreement could be expected. The remarks on p. 949 in regard to the difficulty of preventing loss in the incineration for calcium oxide should be borne in mind in judging the analyses. The salt probably carries down more than $6H_2O$, since the contraction of the precipitate is very great and the loss upon prolonged drying of the finely powdered salt in the air is considerable, even after the salt is apparently dry. Since the salt seems to have no crystalline structure, it is questionable whether the amount of water is a fixed quantity; moreover, the avidity with which the dried salt takes up moisture makes accurate weighing impossible, and the main difficulty in getting concordant analyses is in the drying of the salt because some temperature must be arbitrarily chosen below which the loss is supposed to be adhering water and not water of constitution.

To prepare basic or tribarium meconate, we brought together in solution 8.263 grams of crystallized meconic acid (titrating 106.7 per cent. purity, owing to loss of some of the crystal water) and 400 cc. barium hydroxide solution which was $2.603 \times N/10$. The reaction-mixture was diluted to 1 liter. A voluminous, flocculent, yellow precipitate fell at once and the mother-liquor was neutral. After standing in the mother-liquor for a week, the yellow precipitate had become crystalline. It should be noted that the tricalcium meconate was allowed to stand similarly but failed to become crystalline. The precipitate after drying for a week at 60° weighed 15.12 grams. A small amount was lost through the tearing of a filter; this is estimated at 0.1 gram, so the true yield was something over 15.2 grams. The mother-liquor contained 0.222 gram Ba (as determined by precipitating $BaSO_4$ and weighing) which would indicate a solubility of about 0.5 gram of tribarium meconate per liter. Calculating the theoretical yield of

salt from the amount of barium actually carried down we get 15.37 grams for the formula $Ba_3(C_7HO_7)_2.6H_2O$.

That meconic acid behaves as a tribasic acid towards calcium and barium seems certain from the above work. The salts formed are light yellow, amorphous precipitates, the barium meconate becoming crystalline on long standing in contact with the mother-liquor. Both are only very sparingly soluble in water as in most ordinary solvents. Their composition is expressed approximately by the formulas $Ca_3(C_7HO_7)_2+6H_2O$ and $Ba_3(C_7HO_7)_2+6H_2O$. This, moreover, is nothing unusual, for many organic acids are known which contain, in addition to the carboxyl group, a hydroxyl group, the hydrogen atom of which may be replaced by certain metals. Salicylic acid, for example, forms a calcium salt having the formula $Ca(C_6H_4OCOO)$, analogous to the tricalcium meconate. In fact, it seems strange that we have not been able to find any analyses of the tricalcium and barium salts when the analogous compounds of meconic acid with lead and silver were studied early in the history of the acid and their nature understood. To be sure, they are not very attractive bodies to work on, being slimy precipitates of large volume and varying water content, probably also tending to become basic by the prolonged action of water. Indeed this behavior towards boiling water is one of Dott's[1] arguments in favor of his belief that meconic acid is "dibasic." He found that the percentage of silver in the silver salt increased by boiling the salt with water for several hours. Also that the lead salt prepared under various conditions contained different amounts of lead and drew the inference that these salts were only dibasic salts more or less basic. Later work has shown beyond much doubt that the acid contains two carboxyl groups and in that sense is "dibasic," but that there is also a hydroxyl group with phenolic tendencies to salt formation. We do not consider that the facts mentioned by Dott constitute the slightest objection against granting the tribasic compounds of silver, lead, calcium and barium with meconic acid the rank of true salts. In fact, if the accepted formula for the acid is correct, we should predict just such behavior.

SUMMARY.

In the assay of opium by the U. S. P. 1890 process, a yellowish scaly coating was noticed on the bottom of the flasks which evidently was not morphine. This body was isolated and analyzed.

[1] *Chem. News*, 1880, p. 576.

It was also prepared artificially and analyzed. The results show it to be a double salt of meconic acid with calcium and ammonium, the calcium coming from the opium and the ammonia being added in the process of assay. Its composition according to our analyses is represented by the formula $CaNH_4C_7HO_7.2H_2O$ or $CaNH_4C_7HO_7.3H_2O$ and it is apparently a perfectly definite salt under the conditions of the assay procedure, namely, the presence of meconic acid, excess of ammonia, and scarcity of calcium. This salt or some similar salt was known to Robiquet, but we have not found any formula assigned to it in the literature.

The importance of the salt in the assay process, lies in the fact that if a precipitate of morphine alkaloid containing it as impurity is titrated with standard sulphuric acid to determine the purity of the morphine, the result is always too high owing to the fact that the calcium ammonium meconate consumes nearly 0.25 as much acid as morphine itself. A table is given showing the magnitude of the error in actual assays.

In this work the question arose as to whether the hydrogen of the hydroxyl group in meconic acid possesses acid properties towards barium and calcium as it does towards silver and lead and perhaps other bases forming insoluble compounds. This is shown to be the case and salts having a composition corresponding approximately to the formulas $Ca_3(C_7HO_7)_2.6H_2O$ and $Ba_3(C_7HO_7)_2.6H_2O$ have been prepared. The amount of water in these salts, however, is uncertain. The statement is made in Gmelin-Kraut's "Handbuch der Organischen Chemie" (1859) and in Fehling's "Handwörterbuch" that "barium meconate" is readily soluble in an excess of barium hydroxide and this is attributed to Liebig. We have not been able to find this statement in the original articles of Liebig on meconic acid. We find that dibarium meconate as well as tribarium meconate are nearly insoluble in a solution of barium hydroxide. We give our analyses and preliminary formulas for these tribasic salts because they are apparently not described in the literature. The dicalcium and dibarium salts have been recently prepared by Peratoner and Tamburello[1] by decomposing meconic acid exactly neutralized with ammonia with calcium and barium chlorides respectively, and are described as *yellow* precipitates having the formulas $CaC_7HO_7.4H_2O$ and $BaC_7HO_7.3H_2O$. We obtained a white calcium salt by decom-

[1] Peritoner and Tamburello: Abst. in *Centrbl.*, **1**, 45 (1904).

posing meconic acid exactly neutralized with sodium hydrate and a white barium salt by mixing solutions of barium hydroxide and meconic acid in the proportion of one molecule of barium hydroxide to one molecule of acid. The analysis of the barium salt for barium and the loss of water on drying correspond fairly well with the above formula. No analyses were made of the calcium salt.

Upon attempting to prepare monobarium meconate by mixing meconic acid and barium hydroxide we obtained a salt identical with the dibarium meconate and free meconic acid remained in the mother-liquor.

Our experience with meconic acid leads us to believe that it titrates quite accurately as a dibasic acid towards N/10 NaOH, using blue litmus paper as indicator outside of the solution.

The various salts of barium and calcium with meconic acid were studied first hand in order to throw light on the composition of the unknown "scale" of the assays. None of the combinations of calcium and meconic acid without ammonia possess the properties characteristic of the "scale," ammonium calcium meconate.

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The stars indicate the publications in which the articles were available to us. Double stars indicate articles with especial reference to salts of meconic acid or bearing upon salt formations. In general, it may be said that the literature before Liebig's discovery in 1833[1] of the true relationship between meconic, comenic and pyrocomenic (synonymous with pyromeconic) acids is of little importance except historically.

Beilstein (Vol. II, p. 2041) gives a reference[2] to an article by Liebig which is incorrect. The reference given is to an article by Blanchet and Sell on an entirely different subject and there is no other article in that volume by Liebig on meconic acid. The above list includes some references to comenic and pyrocomenic acids which were examined for information on the parent acid.

MALLINCKRODT CHEMICAL WORKS,
ST. LOUIS.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE DETECTION AND DETERMINATION OF ETHYL AND METHYL ALCOHOLS IN MIXTURES BY THE IMMERSION REFRACTOMETER.

BY ALBERT E. LEACH AND HERMANN C. LYTHGOE.

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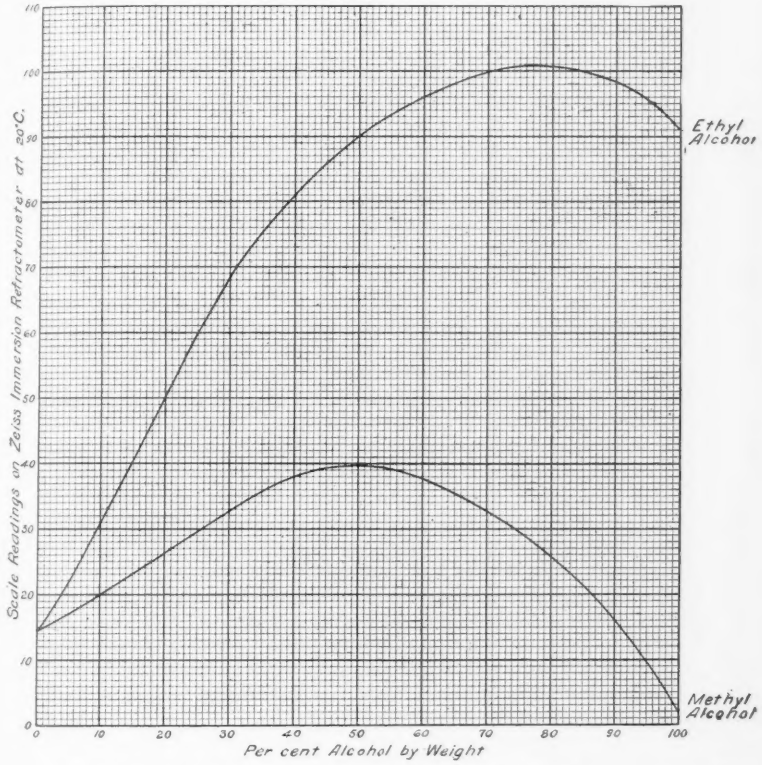
THE USE of wood alcohol in various preparations which come within the domain of the public analyst for examination is apparently on the increase. It is especially to be looked for as an adulterant in medicinal preparations, liniments, tinctures, and in all varieties of flavoring and other extracts high in alcohol. In Massachusetts we have found methyl alcohol in various pharmaceutical preparations, such as tincture of iodine, and in lemon and orange extracts.

Existing methods for the detection of wood alcohol, with one or two exceptions, are extremely unsatisfactory. Most of the older methods such, for example, as the potassium permanganate

[1] *Ann. Chem.*, **7,** 237.

[2] *Ibid.*, **5,** 286 (1833).

test, depend upon the presence of acetone in the methyl alcohol. With the improved refining processes used at the present day wood alcohol is readily obtainable free from more than traces of acetone, so that it is impossible to distinguish it from ethyl alcohol by its odor. Crude wood alcohol with acetone present in marked degree is frequently capable of being indicated even in mixture with ethyl alcohol by the sense of smell. It is the refined or de-



odorized methyl alcohol, sold under a variety of trade names, such as Columbian spirits, Hastings spirits, Colonial spirits, purified wood alcohol, etc., that one finds as an adulterant of tinctures, extracts and beverages.

The most practical method hitherto used for the detection of

methyl alcohol is that of Mulliken and Scudder,[1] which depends on the oxidation of the methyl alcohol in the sample to formaldehyde by the use of a red-hot spiral of copper wire, using, however, the hydrochloric acid and milk test for the detection of formaldehyde in the oxidized solution.[2]

Attention is further called to the German official process of Windisch,[3] a color reaction depending on the transformation of the methyl alcohol to methyl violet.

Methods for the quantitative determination of wood alcohol are even more rare. Duprey[4] has suggested a method of concentrating the alcohol by repeated distillation, after which part of the final distillate is oxidized to acetic acid, the latter being titrated with alkali, while the alcohol is determined in the other portion of the distillate from the specific gravity. Both methods with pure ethyl alcohol should give concordant results, whereas in presence of methyl alcohol a lower result is obtained by the oxidation process.

The specific gravity of absolute methyl and ethyl alcohol is practically identical, and it is also true that when mixed with varying proportions of water the specific gravity of both alcohols is so nearly the same (with the same proportions of water in each) that the same tables for computation of percentage of alcohol from the specific gravity may be used in one case as in the other.

A very important physical constant, however, which we have found to differ most widely in the two alcohols is the index of refraction, and it is on this property that we base our method for the detection and determination of methyl alcohol.

We use for this purpose the immersion refractometer of Zeiss. This instrument was fully described in a former paper by us.[5] To illustrate the wide difference in refraction between the two alcohols, the strongest commercial ethyl alcohol found on the market (the alcohol of the U. S. Pharmacopoeia, which contains 91 per cent. of absolute alcohol by weight) gives a reading with the immersion refractometer of 98.3° at 20° C., while the reading of methyl alcohol of 91 per cent. strength by weight is 14.9°. Fifty per cent. ethyl alcohol by weight has a refraction on the immersion re-

[1] *Am. Chem. J.*, **24**, 444 (1900): this Journal, **27**, 892.

[2] Ann. Rept. Mass. State Board of Health, 1897, p. 558; Leach: "Food Inspection and Analysis," p. 666.

[3] *Vereinbar. z. Unters. v. Nahr. u. Genussm.*, Heft II, p. 130.

[4] *Analyst*, **1**, p. 4.

[5] This Journal, **26**, 1196 (1904).

TABLE I.—PERCENTAGE BY WEIGHT OF ETHYL AND METHYL ALCOHOLS CORRESPONDING TO SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20° C.

Scale reading. 20° C.	Per cent. alcohol by weight. Methyl alcohol.	Ethyl alcohol.	Scale reading. 20° C.	Per cent. ethyl alcohol by weight.	Scale reading. 20° C.	Per cent. ethyl alcohol by weight.
0...			40...	14.73	80...	38.82
1...			41...	15.23	81...	39.64
2...	100.00		42...	15.73	82...	40.64
3...	99.33		43...	16.23	83...	41.64
4...	98.69		44...	16.73	84...	42.75
5...	98.06		45...	17.23	85...	43.75
6...	97.44		46...	17.73	86...	44.75
7...	96.80		47...	18.23	87...	46.00
8...	96.13		48...	18.73	88...	47.25
9...	95.42		49...	19.23	89...	48.38
10...	94.71		50...	19.73	90...	49.62
11...	94.00		51...	20.25		
12...	93.28		52...	20.77	91...	50.87 100.00
13...	92.55		53...	21.29	92...	52.66 99.00
14...	91.75		54...	21.81	93...	54.00 98.00
15... 1.34	90.92	0.33	55...	22.33	94...	55.80 97.00
16... 3.00	90.08	1.00	56...	22.85	95...	57.60 96.00
17... 4.67	89.25	1.62	57...	23.38	96...	59.60 95.00
18... 6.34	88.45	2.25	58...	23.90	97...	61.75 94.00
19... 8.00	87.64	2.93	59...	24.43	98...	64.00 91.60
20... 9.67	86.73	3.56	60...	24.94	99...	66.75 88.50
21... 11.34	85.80	4.19	61...	25.50	100...	70.00 85.50
22... 13.00	84.80	4.82	62...	26.06	101...	75.00
23... 14.67	83.60	5.39	63...	26.60		
24... 16.17	82.40	5.94	64...	27.15		
25... 17.72	81.20	6.50	65...	27.71		
26... 19.33	80.00	7.06	66...	28.29		
27... 20.93	78.75	7.58	67...	28.88		
28... 22.47	77.43	8.09	68...	29.44		
29... 23.96	76.00	8.64	69...	30.00		
30... 25.50	74.57	9.20	70...	30.71		
31... 27.18	73.14	9.76	71...	31.47		
32... 28.67	71.50	10.32	72...	32.21		
33... 30.33	70.00	10.87	73...	32.93		
34... 32.00	68.00	11.43	74...	33.69		
35... 33.50	66.00	11.99	75...	34.43		
36... 35.16	64.00	12.54	76...	35.09		
37... 37.00	62.00	13.10	77...	35.99		
38... 40.00	59.75	13.64	78...	37.00		
39... 43.93		14.19	79...	37.90		

fractometer of 90.3°, while the same strength (50 per cent.) of methyl alcohol refracts on the instrument at 39.8°, all readings being made at 20° C. From this wide variation it is readily seen that there is no trouble in detecting even small amounts of methyl alcohol in mixtures. Table I shows the percentage by weight at 20° C. of the two alcohols corresponding to each degree of scale reading on the refractometer.

The difference in refraction between the two alcohols varies considerably for different strengths. In the case of methyl alcohol, starting at zero (or water containing no alcohol) at which the reading on the immersion at 20° is 14.5, the refraction gradually increases with increasing strength of methyl alcohol up to about 50 per cent. of the latter by weight, where the refraction reaches its maximum, after which for higher strengths of methyl alcohol it drops quite rapidly until at 100 per cent. the refraction is but 2.0.

In the case of ethyl alcohol, starting, as before, with pure water and increasing the strength of the solution in alcohol, the refraction increases quite rapidly up to solutions of about 75 per cent. strength, where it then drops slightly, but by no means to such an extent as in the case of methyl alcohol. It will thus be seen that by far the widest variations in refraction between the two alcohols take place above 50 per cent. in strength.

From the peculiar shape of both alcohol curves, rising gradually to a maximum and then falling, no confusion should be caused by the fact that in some cases one scale reading may correspond to two different percentages of strength of the same alcohol.

The detection of wood alcohol by this method is comparatively simple and consists in submitting to refraction with the immersion refractometer the distillate which one makes for the determination of ethyl alcohol in the regular manner in alcoholic beverages, essences, tinctures, extracts, or whatever may be the nature of the substances to be examined. If the refraction of the liquid shows the percentage of alcohol agreeing with that obtained from the specific gravity in the regular manner, it may safely be assumed that no methyl alcohol is present. If, however, there is an appreciable amount of methyl alcohol the low refractometer reading will at once indicate the fact. If the absence in the solution of other refractive substances than water and the alcohols is assured

this qualitative test by difference in refraction is conclusive, but if there is doubt a confirmatory test by the Mulliken and Scudder method[1] should be made.

TABLE II.—SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20° C. CORRESPONDING TO EACH PER CENT. BY WEIGHT OF ETHYL AND METHYL ALCOHOL.

Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Ethyl alcohol.	Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Ethyl alcohol.	Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Ethyl alcohol.
0...	14.5	14.5	34...	35.2	74.4	68...	34.0	99.4
1...	14.8	16.0	35...	35.8	75.8	69...	33.5	99.7
2...	15.4	17.6	36...	36.3	76.9	70...	33.0	100.0
3...	16.0	19.1	37...	36.8	78.0	71...	32.3	100.2
4...	16.6	20.7	38...	37.3	79.1	72...	31.7	100.4
5...	17.2	22.3	39...	37.7	80.2	73...	31.1	100.6
6...	17.8	24.1	40...	38.1	81.3	74...	30.4	100.8
7...	18.4	25.9	41...	38.4	82.3	75...	29.7	101.0
8...	19.0	27.8	42...	38.8	83.3	76...	29.0	101.0
9...	19.6	29.6	43...	39.2	84.2	77...	28.3	100.9
10...	20.2	31.4	44...	39.3	85.2	78...	27.6	100.9
11...	20.8	33.2	45...	39.4	86.2	79...	26.8	100.8
12...	21.4	35.0	46...	39.5	87.0	80...	26.0	100.7
13...	22.0	36.9	47...	39.6	87.8	81...	25.1	100.6
14...	22.6	38.7	48...	39.7	88.7	82...	24.3	100.5
15...	23.2	40.5	49...	39.8	89.5	83...	23.6	100.4
16...	23.9	42.5	50...	39.8	90.3	84...	22.8	100.3
17...	24.5	44.5	51...	39.7	91.1	85...	21.8	100.1
18...	25.2	46.5	52...	39.6	91.8	86...	20.8	99.8
19...	25.8	48.5	53...	39.6	92.4	87...	19.7	99.5
20...	26.5	50.5	54...	39.5	93.0	88...	18.6	99.2
21...	27.1	52.4	55...	39.4	93.6	89...	17.3	98.9
22...	27.8	54.3	56...	39.2	94.1	90...	16.1	98.6
23...	28.4	56.3	57...	39.0	94.7	91...	14.9	98.3
24...	29.1	58.2	38...	38.6	95.2	92...	13.7	97.8
25...	29.7	60.1	59...	38.3	95.7	93...	12.4	97.2
26...	30.3	61.9	60...	37.9	96.2	94...	11.0	96.4
27...	30.9	63.7	61...	37.5	96.7	95...	9.6	95.7
28...	31.6	65.5	62...	37.0	97.1	96...	8.2	93.9
29...	32.2	67.2	63...	36.5	97.5	97...	6.7	94.0
30...	32.8	69.0	64...	36.0	98.0	98...	5.1	93.0
31...	33.5	70.4	65...	35.5	98.3	99...	3.5	92.0
32...	34.1	71.7	66...	35.0	98.7	100...	2.0	91.0
33...	34.7	73.1	67...	34.5	99.1			

[1] *Loc. cit. supra.*

Not only can methyl alcohol be thus readily detected, but the amount may be approximately and in some cases very accurately determined. Addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount present. Hence the quantitative calculation may be readily made by interpolation in Table II, which follows, using the figures for pure ethyl and methyl alcohol of the same alcoholic strength as the sample. The degree of accuracy of this calculation varies with the strength of alcohol. For instance, with an alcoholic strength of 10 per cent. there is less exactness than at 50 per cent. strength, where 1 per cent. or even less can be readily determined. From this point on the delicacy of the process naturally increases, until at 90 per cent. strength 0.1 per cent. of methyl alcohol may be determined with accuracy.

Table II shows the refraction on the immersion refractometer corresponding to each percentage of alcohol, both ethyl and methyl by weight, all readings being taken at exactly 20° C. This table will show at a glance whether a solution of given strength of alcohol as determined from the specific gravity contains ethyl or methyl alcohol, or is a mixture of the two.

The fact should be borne in mind that in the examination of flavoring extracts it is difficult to so completely separate out the volatile oils as to prevent minute traces from appearing in the distillate. These, and indeed any volatile substances present in marked degree, appreciably affect the accuracy of the quantitative results, though mere traces do not cause serious error. The presence of notable amounts of acetone exercises also a marked effect, but the purified wood alcohol commonly used as an adulterant contains so little acetone that it may ordinarily be neglected in expressing approximate results. Pure acetone refracts considerably lower than ethyl alcohol.

Two or three examples of actual cases as found in the routine inspection of foods and drugs in Massachusetts will best illustrate the method of calculation. For determination of total alcohol from the specific gravity, Hehner's alcohol tables were used.

(1) A lemon extract found by the polariscope to contain 4.9 per cent. of lemon oil by volume and 90.20 per cent. of alcohol by volume at 15° was freed from lemon oil by diluting four times with water, treating with magnesia in the regular manner and filtering.

A measured portion of the filtrate was then distilled and the distillate made up to the measured portion taken. This distillate was found to have a specific gravity of 0.9736, corresponding to 18.38 per cent. alcohol by weight,[1] and to have a refraction of 35.8 on the Zeiss immersion refractometer.

By interpolation in Table II the readings of ethyl and methyl alcohol corresponding to 18.38 per cent. alcohol are 47.2 and 25.4 respectively, the difference being 21.8. $47.2 - 35.8 = 11.4$. $(11.4 \div 21.8)\,100 = 52.3$. In this case 52.3 per cent. of the alcohol present was methyl.

(2) An orange extract was found with 1.5 per cent. of orange oil and 83.2 per cent. of alcohol by volume at 15° C. The specific gravity of the one-fourth strength distillate, freed from oil as in the case of the lemon extract, was 0.9754, corresponding to 16.92 per cent. alcohol by weight Refraction of the distillate at 20° C. was 42.0. Readings of ethyl and methyl alcohol of 16.9 strength are, according to Table II, 44.3 and 24.5 respectively. Difference, 19.8. $44.3 - 42 = 2.3$. $(2.3 \div 19.8)\ 100 = 1.2$. Thus, 1.2 per cent. of the alcohol present was methyl.

(3) 6.3 cc. of tincture of iodine, after titration with N/10 sodium thiosulphate (in the regular manner for determining its strength according to the U. S. Pharmacopoeia), were neutralized with N/10 sodium hydroxide and distilled, collecting 25.2 cc. of the distillate, corresponding to a dilution of 1 :4 of the sample. The distillate contained 20.92 per cent. alcohol by weight, refraction 27.5 at 20° C., indicating 99 per cent. of the alcohol to be methyl. There is no doubt that the alcohol in this case was entirely methyl, the slightly high refraction of the distillate being due to the presence of a slight amount of volatile substance, formed by decomposition of the tincture of iodine.

The accuracy of the method is shown in a general way by a series of experiments, the results of which are tabulated as follows:

[1] Our methyl-ethyl alcohol tables being most conveniently worked out on the weight-per cent. basis, the per cent. by weight rather than by volume of the dilute distillate is here taken. Percentage of total alcohol in the extract as well as of lemon oil we commonly express by volume. In this case, the specific gravity 0.9736 corresponds to 22.55 per cent. alcohol by volume. The per cent. by volume of total alcohol in the extract, 90.20 at 15° C., is found by multiplying 22.55 by 4 to correct for the dilution.

TABLE III.—READINGS OF EXPERIMENTAL MIXTURES OF METHYL AND ETHYL ALCOHOLS.

			Methyl alcohol.		Ethyl alcohol.	
Sp. gr. 15° C.	Per cent. alcohol by weight.	Scale reading. 20° C.	As prepared. Per cent.	As found. Per cent.	As prepared. Per cent.	As found. Per cent.
0.8190	91.36	33.9	68.52	69.88	22.84	21.48
0.8190	91.36	54.9	45.68	47.41	45.68	44.95
0.9239	47.41	51.9	35.56	35.42	11.85	11.99
0.8190	91.36	76.3	22.84	23.75	68.52	67.61
0.9326	43.43	62.4	21.71	21.38	22.71	22.05
0.9643	25.64	37.2	19.23	19.76	6.41	5.88
0.9207	48.86	77.5	12.21	11.77	36.65	37.09
0.9753	17.00	34.0	8.50	8.92	8.50	8.08
0.9666	23.92	50.2	5.98	6.48	17.94	17.44

SOME OBSERVATIONS ON THE DEPOSITION OF ALLOYS FROM MIXED SOLUTIONS.[1]

BY CHARLES B. JACOBS.

Received June 17, 1905.

RECENTLY the writer had occasion to make a simultaneous deposition of two metals, zinc and nickel, under conditions in which it was impossible to use any of the well-known methods.

The current strength permitted could not be great enough to prevent secondary action of the electropositive metal on the solution of the other, for it would then have resulted in a pulverulent deposit, and the physical structure of the deposit required prohibited anything but a strongly adherent, finely crystalline metal. Neither could cyanide solutions or alkaline solutions of any kind be used, as the deposited alloy was intended to receive a lithographic transfer, and any trace of cyanide solution or alkali acted on the transfer ink and destroyed the fine dots and lines of the work. If the deposited metal were washed sufficiently to rid it of the last traces of cyanide or alkali it became oxidized in spots. These oxidized spots refused to permanently hold the ink from the transfer paper.

Moreover, the composition of the alloy required did not permit of having a small proportion of the more electronegative metal in the bath.

It therefore became necessary to devise a means of plating zinc and nickel simultaneously without the use of cyanide solu-

[1] Read at the Buffalo Meeting of the American Chemical Society.

tions, without maintaining an abnormal current density and with a comparatively large amount of zinc, the electronegative metal, present in the solution.

It soon became apparent that neutral sulphate solutions of zinc and nickel were the ones most suitable for the purpose, to which we found we might add varying proportions of ammonium sulphate and ammonium chloride to aid in regulating the internal resistance of the bath.

The question of anodes was next taken into consideration. An attempt was made to have anodes of zinc and nickel cast of the desired composition for the alloy. This was frustrated on account of the high melting-point of the nickel and the impossibility of obtaining uniform results in the casting. Double anodes were then tried, one of zinc and one of nickel as pure as could be obtained. This worked fairly well for a short time, but a wide departure from the original alloy deposited soon made itself apparent. On examination of the bath and the deposited metal both were found to be running very much higher in nickel than was intended, with a corresponding deficiency in zinc.

Without going into the details of the failures of the many schemes proposed for maintaining the correct proportions of nickel and zinc in our baths, and consequently in our deposited metal, I will only say that it required the better part of six months to solve the problem and reduce it to commercial practice.

A careful consideration of the fundamental laws governing electrolysis with respect to the deposition of metals and a practical application of these laws to fit our peculiar conditions, finally led to the commercial solution of the problem. Since the anodes and the deposited metal were of the same composition we were limited in the electromotive force of the plating bath only by the current density that the cathode surface would stand without yielding a bad deposit.

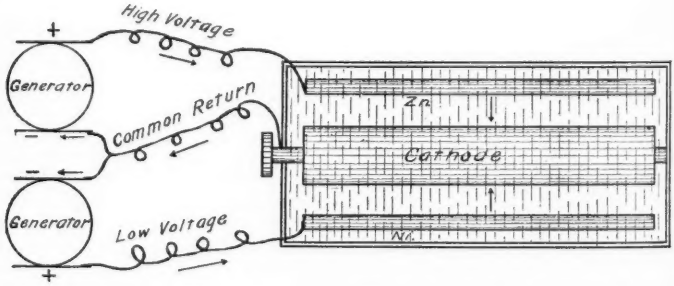
The consecutive separation of metals from mixed solutions in the ascending scale of their electropositiveness, however, was our chief difficulty. Since there is a difference of voltage necessary to decompose the nickel and zinc salts amounting to about 0.35 of a volt in favor of the nickel, it was impossible at the same voltage to prevent the nickel from increasing in amount both in

the bath and in the deposit. This very difficulty gave the clue to the solution of the problem.

The electrochemical equivalents show that 1.0994 grams of nickel and 1.2112 grams of zinc are deposited per hour by a current of 1 ampere, and it follows from Ohm's law that the strength of current in amperes depends on the electromotive force between the cathode and the anodes.

It only remained to find a method of maintaining the proper difference in voltage between the two anodes and the cathode to have a perfect regulation of the amount of the two metals deposited on the cathode. This was accomplished by the use of two generators running at different voltages, one for the zinc and one for the nickel anode, the current returning through the cathode in the bath by a common third leg to the generators. The plating baths happened to be so designed as to lend themselves readily to the scheme. The inside dimensions of the baths were 72 inches in length, 36 inches in width, and 22 inches in depth. The cathode surface was composed of a copper tube $13\frac{1}{2}$ inches in diameter and 60 inches long. It was fastened to a pair of contact heads directly in the center of the ends of the bath. These heads revolved with the tube at the rate of 2 to $2\frac{1}{2}$ revolutions per minute.

The circuit from the generators to the bath and return was as shown in the sketch.



This arrangement made it possible to hang the zinc anode on one side and nickel anode on the other of the revolving cathode and place them at variable distance, in order to regulate the internal resistance of the bath between the cathode and either anode.

On account of the tendency of the nickel to deposit at lower voltage and also for the reason that a greater proportion of zinc than nickel was required in the alloy, the generator on the zinc side was run at the high voltage.

It was now possible to find the voltage which in relation to the internal resistance of the bath would give the proper relative proportions of zinc and nickel in the deposit, with no more than the ordinary proper attention required in the care of any plating-bath to keep these relative proportions fixed.

Sixteen plating-baths of the dimensions given above were equipped with this method which, whether correctly named or not, became known as the "Three Phase Plating System."

In the commercial equipment of the plating-room three sets of bus bars were run along the wall. All the zinc anodes were tapped into the high voltage bar and all of the nickel anodes into the low voltage bar, while the cathodes were all led to the common third bar returning to the generators.

Plating on sheets of metal as well as on the copper tubes was carried out by this method. Sheets of zinc 60 inches by 45 inches were strapped around a revolving cathode by means of clamps and turn buckles and a deposit of nickel and zinc thrown upon them. The metal was reguline, firmly adherent, and showed no tendency to peel or crack, after the sheets were taken off the cathode and laid out straight.

The general commercial application of this method of depositing two metals simultaneously upon the same cathode has not been investigated to any great extent beyond the deposition of nickel and zinc.

Some experiments were made on a small scale in the deposition of copper and zinc from sulphate solutions and a composition was obtained which gave a very good-looking quality of yellow brass.

With a cyanide solution, however, and an anode of copper on the low voltage side and zinc on the high side, some very excellent results were obtained on sheets 60 inches by 45 inches. The regulation in the color of the brass was almost perfect, as it was only necessary to fluctuate the voltage on either side to vary the color from a reddish brass running high in copper to a very light brass running high in zinc.

This method offers a much simpler means of regulation of

color and composition than is possible with a brass anode. It also makes it possible to produce from the same bath a great variety of color and composition in brassing work.

THE CHEMISTRY OF ORE DEPOSITION—PRECIPITATION OF COPPER BY NATURAL SILICATES.[1]

BY EUGENE C. SULLIVAN.

Received May 27, 1905.

WORK recently done in the chemical laboratory of the United States Geological Survey shows that natural silicates and especially feldspars enter into reactions of double decomposition with salt solutions at ordinary temperatures more readily than is generally recognized, and it appears possible that not only the importance of feldspars, estimated to make up 60 per cent. by weight of the lithosphere,[2] as precipitants in geological reactions, but also the great superiority of salt solutions over water as disintegrating agents, have not been sufficiently emphasized.

The work in question has suffered interruption for the present, and it is thought desirable to present in very brief outline, at this time, some of the results thus far obtained.

Lemberg[3] showed that sodium chloride solution at ordinary temperature transformed leucite ($KAlSi_2O_6$) partly into analcite ($NaAlSi_2O_6.H_2O$), sodium being substituted for the equivalent quantity of potassium. The reverse substitution took place when analcite was treated with potassium chloride solution.

The reaction

$$KAlSi_2O_6 + NaCl + H_2O \rightleftharpoons NaAlSi_2O_6.H_2O + KCl$$

is similar to the familiar one

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

Provided the mass law holds, equilibrium sets in when the concentrations of the substances have the following relation (formulas in brackets indicate concentrations):

$$[KAlSi_2O_6].[NaCl].[H_2O] = k[NaAlSi_2O_6.H_2O].[KCl],$$

k being the equilibrium constant. As the silicates are both present as solids, their active mass is constant, as is also that of the

[1] Published by permission of the Director of the United States Geological Survey.

[2] F. W. Clarke: Bulletin U. S. Geol. Survey 228, p. 20.

[3] *Z. deutsch. geolog. Ges.*, **28**, 537 (1876).

water; substituting the concentrations of the ions concerned for those of the salts, we have $\frac{[Na^{\cdot}]}{[K^{\cdot}]} = \text{constant}$.

That is, equilibrium is attained when the concentrations of the sodium ion and the potassium ion are in a certain definite ratio. If $Na^{\cdot}$ is present in excess of this ratio solid analcite forms, withdrawing sodium from solution until the equilibrium ratio is established; if $K^{\cdot}$ is present in excess the reverse change takes place, again restoring the same equilibrium. Treating repeatedly with fresh portions of either salt would tend to convert the solid completely into the silicate containing the alkali used.

These considerations apply only in case both solids are allowed free contact with the solution. This might conceivably be prevented by the precipitation of a surface film on the particles of the original solids or by the formation of a layer of partly disintegrated material which the solution will not penetrate.

Way,[1] Eichhorn,[2] Peters, van Bemmelen,[3] and others obtained with soils, kaolin, etc., results precisely similar to those of Lemberg. The finely-divided solids take up base from a salt solution, giving off an equivalent quantity of their own constituents.

Following a suggestion made by Kohler,[4] the present writer first took up the action of kaolin on cupric sulphate solution.[5] Kohler discusses the possibility of a causal relation between the adsorptive capacity of clays and their association with the ores of certain metals, notably copper, adsorption referring to the power ascribed to solids, immersed in a solution, of concentrating the dissolved substances on their surface. Such action would be especially marked in the case of powdered or porous material.

A washed kaolin was used, containing 1.6 per cent. alkali, mostly potassium, and small quantities of calcium, magnesium and sulphates. Microscopic examination showed the presence of undecomposed feldspar.

Among other solids employed, all ground to a fine powder, were:

[1] *Jour. Roy. Agr. Soc.*, **11**, 313 (1850); **13**, 123 (1852).

[2] Pogg. *Ann.*, **105**, 126 (1858).

[3] *Landw. Versuchsstationen*, **21**, 135 (1877); **23**, 264 (1879); **35**, 69 (1888): etc.

[4] Kohler: "Adsorptionsprozesse als Faktoren der Lagerstättenbildung und Lithogenesis," *Z. prakt. Geologie*, **11**, 49 (1903).

[5] The work with kaolin was undertaken at the suggestion of Mr. W. H. Weed, of the Geological Survey, in the hope of throwing light on the formation of Montana copper-ore deposits. The writer is much indebted to Mr. Weed for material and information on the geological side of the work.

Shale from Arizona, consisting largely of kaolin and glauconite and containing 6.74 per cent. K_2O and 0.44 per cent. Na_2O.[1]

Two specimens of orthoclase from San Diego County, California, fairly pure.[2]

Well-crystallized albite from Amelia Court House, Va.[3] Albite from this region is shown by analysis to be almost perfectly pure.

Crystalline microcline from Way's Quarry, near Wilmington, Delaware, also shown by analysis to be very pure.[2]

Pyrite, ground in water to a fine mud, washed with dilute sulphuric acid, water, alcohol, and ether, and dried at 100° C.

The kaolin, shale, and feldspars were subjected to quantitative tests for carbonate; none contained more than an insignificant trace.

To determine the action of a powdered solid on cupric sulphate solution, 25 grams of the powder were added to 50 cc. of the solution (in most cases a 1 per cent. solution of the crystalline $CuSO_4.5H_2O$, containing 0.252 gram copper in 100 cc.) in a flask which had been steamed to remove easily soluble matter from the glass. After being securely stoppered the mixture was allowed to stand for some time with occasional shaking and was then filtered. The perfectly clear filtrate was analyzed.

Some of the results are as follows: The reaction between the silicate and the copper solution is chiefly an exchange of bases, copper undergoing precipitation and an equivalent quantity of other bases (chiefly the alkali and alkaline earth bases) entering the solution. If adsorption takes place, it is in comparatively insignificant amount.

The acidity of the cupric sulphate solution is not changed by contact with the silicates and precipitation of copper. A certain quantity of SO_4 is precipitated with the copper—in several instances about $1SO_4 : 10Cu$. Whether the corresponding amount of cupric sulphate is adsorbed or whether some precipitation of basic sulphate takes place, as is the case when alkali is added to excess of cupric sulphate solution, remains to be determined. The sum of the bases which go into solution is exactly equivalent to the total copper precipitated, less the SO_4 precipitated.

The equilibrium actually attainable is decidedly dependent on

[1] This shale was kindly furnished by Dr. Lindgren of the Geological Survey, who called the writer's attention to its frequent association with cuprite.

[2] Obtained through Mr. W. T. Schaller, of the U. S. Geological Survey.

[3] Kindly furnished by Mr. Wirt Tassin, of the U. S. National Museum.

the grinding; the finer the powder the more copper is precipitated. The action thus apparently takes place only on the surface of the particles.

The shale removed in one case 95 per cent., in another case the total copper from its solution. The solution remained perfectly neutral, K_2O, MgO, CaO, Na_2O and MnO replacing the copper.

The feldspars orthoclase, albite and microcline, ground in the agate mortar, each remove copper from solution to a surprising extent, 25 grams of the powdered solid taking from 60 to 100 mg. copper out of 50 cc. cupric sulphate solution containing 126 mg. copper. This is a greater precipitation than takes place with kaolin and also greater than that caused by an equal weight of pyrite. Results among different substances are, however, only roughly comparable, owing to the impossibility of getting the powders of the same degree of fineness. The feldspars, originally pure white, were given a decided green tinge by the precipitated copper. After a few washings, further treatment with water removed practically no copper at all from the greenish powder.

Cupric sulphate solution is similar to carbonic acid solution in the extent of its action on feldspar. Somewhat more material was dissolved from orthoclase by 1 per cent. cupric sulphate solution than by suspending in water and passing carbon dioxide for twenty hours. Water alone under similar conditions dissolved but a trace.

Work along the line of that described will be continued in this laboratory.

U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C.,
May, 1905.

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

ON AMORPHOUS SULPHUR: III. THE NATURE OF AMORPHOUS SULPHUR AND CONTRIBUTIONS TO THE STUDY OF THE INFLUENCE OF FOREIGN BODIES ON THE BEHAVIOR OF SUPERCOOLED MELTED SULPHUR.[1]

BY ALEXANDER SMITH AND WILLIS B. HOLMES.

Some Facts about Amorphous Sulphur Previously Established with More or Less Definiteness.—Insoluble or amorphous sulphur seems

[1] A preliminary paper, including some of the present results, appeared in the *Ber.*, 35, 2992 (1902). The experiments were all made before the work described in the

to have been first isolated, examined and described with some care by Deville.[1] The work of previous observers justifies the following conclusions in regard to this modification of sulphur: It is (1) formed in increasing amounts as the temperature rises, and diminishes in quantity as the temperature once more falls. It is thus (2) generated by an endothermal action from soluble sulphur, and (3) at ordinary temperatures is, therefore, less stable than crystalline sulphur.

The following are briefly the facts which support these conclusions:

(1) Amorphous sulphur can be obtained only when the melted sulphur is chilled rapidly. When heated sulphur is allowed to cool slowly little or no insoluble sulphur is ever found. This fact was shown particularly clearly by a few experiments made by Küster,[2] and is further supported by many observations described in the present paper.

(2) The higher the temperature at which the sulphur has been held before being quenched the larger, in general, is the proportion of insoluble sulphur obtained. Thus Moitessier,[3] in connection with his measurements of the coefficient of expansion of melted sulphur, believing that the variation in the value of the coefficient with change in temperature was due to changes in the proportion of insoluble sulphur present, made a series of estimations of the insoluble sulphur obtainable by quenching from various temperatures. His percentages of insoluble sulphur were as follows:

130°.	143°.	148.6°.	159.9°.	167.4°.	179.4°.	213.5°.	249.9°.	284.9°.	440°.
0	0	2.54	7.03	14.77	22.60	27.09	26.31	29.31	30.27

These data are not quoted in chemical works of reference, and the results of Berthelot's experiments[4] are more familiar to chemists. Berthelot gives the following table:

Temperature.	130–140°.	155°.	163°.	170°.	185°.	205°.	230°.
Per cent. insoluble sulphur...	None	Trace	Very little	25	29	29	30

preceding paper, No. II (this Journal, **27**, 797), was done. They form a small part of an extensive series made in the effort to discover the reason of the peculiarities in the behavior of sulphur and are for the most part chosen for publication because they bear more or less directly upon the final conclusion in regard to the nature of amorphous sulphur.

[1] *C. R.*, **26**, 117 (1848).

[2] *Z. anorg. Chem.*, **18**, 365 (1898).

[3] *Memoires de l'Acad. de Montpelier*, **6**, 107 (1864); Cf. Smith, Holmes and Hall: "On Amorphous Sulphur, II," this Journal, **27**, 797.

[4] *Ann. Ch. Ph.* (3), **49**, 481-2 (1857).

These figures are misleading because they give the false impression that there is almost no insoluble sulphur obtainable below 170°, and constant, large amounts about 170°. The work of the present paper (section II) confirms Moitessier's measurements.

(3) The higher the temperature to which the sulphur has been heated the lower, in general, is the temperature at which it freezes. Schaum[1] examined this phenomenon. The work was not done with sufficient thoroughness, however, to justify his inference, *viz.*, that the freezing-point was depressed by dissolved amorphous sulphur by amounts proportional to the quantities of the latter. He observed the freezing-points, simply, and did not simultaneously estimate the insoluble sulphur present. The relation between the temperature of freezing and the amount of dissolved amorphous sulphur was later established conclusively by the quantitative measurements of Smith and Holmes,[2] and shown to be expressed by Raoult's law. In the light of this relation, now determined, Schaum's observations lead to the conclusion that the higher the temperature to which sulphur has been heated the larger the proportion of insoluble sulphur it contains.

One other fact is, or rather was, generally accepted. It is evidently the opinion of many writers that the increase in the viscosity of melted sulphur, which is so suddenly noticeable near 170°, is coincident with the production of the insoluble form and is due to the presence of the latter. Berthelot even states that larger yields of insoluble sulphur are obtainable by chilling from the temperature of maximum viscosity than from any other temperatures, either higher or lower. We have always found smaller amounts below this temperature and larger ones above it, however, and Kastle and Kelley[3] have likewise failed to confirm Berthelot's observation. After we had found that melted sulphur which had been treated with a little gaseous ammonia gave no insoluble sulphur when chilled, but still exhibited the usual increasing viscosity when carried above 170° and resumption of the mobile condition when cooled,[4] it became doubtful for a time whether there was any connection at all between viscosity and the content of insoluble sulphur. It was only after further investigation, described in the preceding and the present papers, that the existence of the connection was re-established.

[1] *Ann. Chem.* (Liebig), **308**, 18 (1899).
[2] *Z. physik. Chem.*, **42**, 469 (1902).
[3] *Am. Chem. J.*, **32**, 488 (1904).
[4] *Ber.*, **35**, 2993 (1902).

The Theory of the Relation of Soluble to Insoluble Sulphur Based on These Facts.—The progressive increase with rising temperature in the proportions of insoluble sulphur, together with the fact demonstrated by the work on the freezing-point that amorphous sulphur can exist dissolved like a foreign body in soluble sulphur, determine one fact about the relation of the two forms. Evidently insoluble sulphur is produced from soluble sulphur by a reversible chemical action and is present, in definite proportions determined by the temperature, in chemical equilibrium with the latter:

$$S \text{ (liquid, soluble)} \rightleftarrows S \text{ (liquid, amorphous)}.$$

This view seems to be held by Küster,[1] Schaum[1] and Duhem,[2] the last mentioned in a wholly theoretical paper.

Berthelot is the chief exponent of a different theory. He found almost no insoluble sulphur below 170°. Above 170° he isolated from the mass when it had been allowed to harden 30 per cent. of insoluble sulphur. He believed that the values at temperatures above 170° fell short of 100 per cent., only because the cooling had not been sufficiently rapid, and endeavored to obtain larger yields by using (1) a fine stream or succession of droplets of boiling sulphur, (2) cooling in ether and other liquids, (3) immediate extraction of the plastic mass. Adding these refinements in succession he obtained with the first alone 61 per cent., with the first and second 71 per cent., with all three 85 per cent. The material used in the last experiment gave 85 per cent. only when extracted while it was plastic. Next day it gave 47 per cent. and two days later 39 per cent. On these results he based the conclusion that the change from soluble to insoluble sulphur takes place *per saltum* near to 171°.

The work of Moitessier and ourselves shows that Berthelot was undoubtedly seriously in error in finding no insoluble sulphur below 170°. On the other hand, it may well be that 100 per cent. of insoluble sulphur is present not far above 170°, but the discussion in the next paragraph will show that Berthelot's method is incapable of demonstrating either that it is or is not so present.

Plastic and Hardened Amorphous Sulphur and the Reasons for Measuring the Proportion of the Latter Only.—When boiling sulphur is rapidly chilled a transparent, yellow, homogeneous, and perfectly plastic material is formed. Let this be assumed to be a

[1] *Loc. cit.*

[2] *Z. physik. Chem.*, **23**, 193 (1897).

solution of soluble and insoluble sulphur in certain proportions. It is evidently impossible to determine what these proportions are, for the properties of soluble and of insoluble sulphur in the plastic condition, separately, cannot be determined. The former cannot be obtained in plastic condition at all and we have no means of knowing whether we ever have the latter alone or not.

After the plastic mass has been allowed to become opaque and hard the proportion of insoluble sulphur contained in it is easily determined by extraction. Once this stage has been reached the further transformation of insoluble into soluble sulphur proceeds very slowly indeed and there is little reduction in the proportion of the former at the ordinary temperature, even when the sample is kept for months.[1] The crude method of extracting the plastic threads or beads at once with carbon disulphide, as used by Berthelot, is open to three objections: (1) Amorphous sulphur, both in the soft and in the hardened conditions, being the less stable form at ordinary temperatures, must be ultimately more soluble than crystalline sulphur.[2] The plastic form must also be more *rapidly dissolved* than is the hardened one. As a matter of fact, in the plastic state sulphur does dissolve pretty freely in carbon disulphide and may be largely recovered by evaporation. (2) The plastic sulphur, when extracted, is found to form an emulsion with the solvent and to be carried in minute drops rapidly through the pores of the thimble. (3) If there is any soluble sulphur present at all it must be covered up by the clinging mass of plastic material and largely escape solution. Berthelot's plan for determining amorphous sulphur in the soft condition is thus wholly futile.

On the other hand, if the transparent, plastic mass is left until it becomes hard, the change is bound to take place in two directions simultaneously. Part of the material, of course, does give quasi-solid, amorphous sulphur. But an undeterminable part must also pass into the soluble crystalline variety. The extraction of the hardened mass does give fairly accurate information in regard to

[1] Deville: *Ann. Ch. Ph.* (3), **47**, 94; Smith and Holmes: *Z. physik Chem.*, **42**, 473.

[2] Doubtless the hardened amorphous sulphur is more soluble, but takes longer than the crystalline variety to reach a state of equilibrium with the solution (see Ostwald: *Handbuch*, **2**, 2, 460; Schaum: *Ann.*, **308**, 28). Some writers describe plastic sulphur as a distinct, soluble variety of amorphous sulphur (see, for example, Magnus: *Pogg. Ann.*, **94**, 308 (1854), and Deville: *Ann. Ch. Ph.* (3), **47**, 94). In the plastic condition amorphous sulphur undoubtedly dissolves more *rapidly* but there is nothing to show that it finally dissolves to a greater extent.

The "soluble amorphous sulphur" formed by precipitation will be shown by Mr. R. H. Brownlee in a forthcoming paper to be wholly finely divided, crystalline, rhombic sulphur.

the proportions of the two kinds finally formed, but it gives only a minimum value for the quantity of insoluble sulphur present before hardening began.[1]

With the exception of a few trials, therefore, all our measurements were made with the final product of hardening and do not pretend to state how much insoluble sulphur was present, either before chilling or immediately afterwards. They are used only for the purpose of *comparing* the effects of variations in the modes of treatment before chilling and the influences of various foreign bodies. Thus from common sulphur, chilled in ice from 448°, after hardening, we obtained 34 per cent. and no more, of insoluble sulphur. On the other hand, when a few bubbles of ammonia were passed before chilling we obtained from the hardened mass by the same process no insoluble sulphur at all. Again, by distilling the sulphur and quenching the burning stream in ice we obtained, after hardening, 51 per cent. From this it may be inferred that the circumstances attending distillation left the plastic sulphur in such a condition that, during the process of hardening, a smaller proportion of it reverted to the crystalline state. Still again, when 2 per cent. of iodine was added before chilling, the hardened product contained 63 per cent. of insoluble sulphur, the largest yield of this form of sulphur which we were able to secure when, after the cycle of changes attending chilling and hardening, the system had reached a stationary condition. As a rule, in all cases, for the sake of comparison, the product, after chilling, was treated in exactly the same way.

Insoluble Sulphur by Precipitation.—It was only after the ex-

[1] Kastle and Kelley, *Am. Chem. J.*, **32**, 484 (1904), studied the shrinkage which occurs when plastic sulphur hardens. They seem to have assumed that this affords a means of measuring the rate of change of plastic sulphur into *crystalline* sulphur. Thus in one experiment (No. 3, p. 487) they assume in their method of calculation, that the shrinkage represented a complete change from 100 per cent. plastic amorphous sulphur to 100 per cent. solid crystalline sulphur, taking place under water at the ordinary temperature within twenty-four hours. Judging from the results of our experiments, made in a similar way, at least 30 per cent. of insoluble sulphur must still have been present. The change in volume from plastic sulphur with sp. gr. 1.95 to hardened amorphous sulphur with sp. gr. 2.05, however, is practically the same as to rhombic sulphur of sp. gr. 2.06–2.07. Professor Kastle, in a private letter, calls attention to the conviction, expressed clearly in the original paper, that plastic sulphur is composed of several molecularly different kinds of sulphur, all of which are amorphous. He believes that *one* or more of these hardens to insoluble amorphous sulphur, while the *others* give only crystalline sulphur. In his experiments he was endeavoring to trace the history of the latter portion only, on the assumption that the change of volume was due exclusively to the crystallization of this part of the material. The authors do not feel that anything at present known compels us to believe that plastic sulphur contains more than one kind of amorphous sulphur. Nor do they feel that it is safe to assume the absence of any change in volume during even the mere hardening of the supposed uncrystallizable constituent.

periments were made in an entirely different way that specimens containing 100 per cent. of insoluble sulphur were obtained. This was by precipitating sulphur from calcium pentasulphide by means of highly concentrated hydrochloric acid. The pentasulphide was added to the acid in order to secure the constant presence of a great excess of the latter from the start. These experiments were done in collaboration with Mr. R. H. Brownlee, and will form the subject of another paper, which has not yet been completed. They are mentioned here to show that when plastic sulphur—for when first precipitated the sulphur is in fluid droplets—is sufficiently finely divided and is in contact with an active acid, it hardens completely to the amorphous state and none of it assumes the soluble form. A similar fineness of subdivision is evidently impossible of attainment in quenching the boiling liquid. When it had thus been ascertained definitely that the conditions necessary for securing 100 per cent. of insoluble sulphur could not be realized by quenching, the effort further to increase the yield by this method was given up.

The Point of View in Which the Results of the Present Experiments Are To Be Interpreted.—The discussion of the various hypotheses which may be used to explain the results of this work on the supercooling of melted sulphur, so far as such discussion can serve any useful purpose, is given later. Since, however, the results themselves cannot be described clearly excepting in terms of some theory, the one finally adopted is used when necessary throughout the paper. It is based upon consideration of all the results, in the light of the facts given in the preceding paper (II) of the series. Briefly, the explanation of the behavior of sulphur is as follows:

There are two liquid states of sulphur which are partially, but only partially, miscible. These are (1) the pale-yellow, mobile liquid which is the normal form from the melting-point of rhombic sulphur up to 160°, and (2) the brown, viscous liquid which is stable above 160°. These we have styled S_λ and S_μ respectively. The latter is present in small amount so soon as the sulphur melts, and is formed in increasing proportions as the temperature rises. The proportion is determined by a reversible action $S_\lambda \rightleftarrows S_\mu$. At 160° the S_λ has become a saturated solution of S_μ, the proportion of the latter at this temperature probably not exceeding 12 per cent. When the temperature is raised beyond this point super-

saturation with S_μ ensues and a new phase consisting of S_μ, in which is dissolved a certain proportion of S_λ, arises. According to the phase rule, with one substance, three phases (two liquids and vapor) can coexist only at a definite temperature—the transition point (160°). Hence above 160° only S_μ, containing amounts of dissolved S_λ which become smaller as the temperature rises, is stable. Rapid heating and the presence or absence of certain foreign substances favor the postponement of the transition of S_λ to S_μ and lead to the familiar variations in the temperature at which the sudden viscosity first appears. Conversely, rapid cooling from temperatures above 160°, particularly when certain foreign bodies are present, favors the postponement of the transition of S_μ to S_λ and hinders or prevents almost entirely the occurrence of the change on which an extensive transformation into S_λ depends. When conditions are favorable, a large proportion of the S_μ may survive to reach the ordinary temperature. The chilled product is then a more or less sticky mass which in time partly reverts to soluble sulphur and partly assumes a quasi-solid, difficultly soluble form. The latter substance is that commonly known as amorphous sulphur. Like all amorphous substances it is a supercooled state of a liquid, namely S_μ. The part which reaches the condition S_λ gives brittle, crystalline, soluble suphur when it solidifies.

I. EXPERIMENTAL METHODS.

The sulphur used was purified by recrystallization from pure carbon disulphide in such a way that a fine crystal-meal was obtained. This was pressed free from the mother-liquor, dried at a gentle heat, and preserved in a loosely corked bottle. Specimens from the same lot were used in each series of similar experiments. Except when otherwise stated 25 grams formed the charge of each tube. The heating to some definite temperature was conducted in open tubes. A large glycerol bath was used for lower temperatures, a paraffin bath for higher ones, diphenylamine vapor at 310° and sulphur vapor at 448°. The supercooling was effected by rapidly pouring the sulphur, or by breaking the tube into powdered ice. Other methods had been found to give yields which were no larger, and were often smaller and always less regular. The experiments on freezing-points[1] had shown that once the temperature had fallen to about 115° the reversion

[1] *Z. physik. Chem.*, **42**, 472.

of the dissolved amorphous sulphur to soluble sulphur was comparatively slow. Thus, since the cooling sulphur was not allowed to form large masses, only a few seconds elapsed before the lowering in temperature requisite to arrest reversion had been attained. When the proportion of amorphous sulphur was small, the product became hard in a few hours and the amount of insoluble sulphur found by extraction closely corresponded to the amount which had actually been present before the chilling began. The freezing-point experiments, which involved amounts from zero up to 5.5 per cent., show that the results were literally quantitative within that range. When, on the other hand, a high temperature had been used, the supercooled mass was often of the familiar elastic description. In such cases the hardening occupied two days or more and, although 30-63 per cent. of insoluble sulphur was contained in the final product, the total amount of S_μ in the material at the plastic stage, not to speak of the liquid before the cooling began, must have been much greater (see preceding paragraph). This uncertainty, and the further fact that a longer time must have elapsed before 115° was reached and the danger of reversion to the soluble form was past, makes caution necessary in the interpretation of the data in regard to sulphur supercooled from very high temperatures. These data are used, therefore, only for comparing the effect of variables other than temperature itself.

Except where otherwise stated, the supercooled mass, after it had become hard, was pulverized and passed through a fine sieve, in order to secure uniform physical condition in the samples used for extraction. The solvent employed was carbon disulphide. Comparable results were obtained by using equal weights (10 grams) in the same state of subdivision and removing the soluble sulphur each time by the same number of fillings (five) of a Soxhlet extractor. The extractions were made in duplicate in each case. Correction for the quantity of insoluble sulphur dissolved at the same time was made as described in the previous paper, where also the experiments testing the accuracy of this method of estimating amorphous sulphur are described.[1]

II. RESULTS OF SUPERCOOLING ORDINARY SULPHUR, THAT IS, SULPHUR WHICH HAS ACQUIRED TRACES OF SULPHUR DIOXIDE, OR SULPHURIC ACID, BY EXPOSURE TO THE AIR.

Each of the results given below was obtained by taking the aver-

[1] *Z. physik. Chem.*, **42**, 474.

age of three or four experiments. Preliminary experiments showed that three hours were required for the attainment of the maximum proportion of insoluble sulphur at the lower temperatures. The individual observations varied in a most disturbing manner, the highest showing sometimes 0.5 per cent. of insoluble sulphur more than the lowest. The results at 448° showed exceptional irregularity, the individual percentages[1] being 31.8, 36.6, 36.1, 31.8. This variation could not be removed by stirring or any other expedient so long as common sulphur was used alone. Trial showed that two tubefuls of sulphur taken from the same lot, heated side by side for the same length of time and cooled simultaneously in the same manner, sometimes gave percentages of amorphous sulphur 0.5 apart. The same experimental method was found to give concordant results in other series, *e. g.*, that in which iodine was present (section IV). The results, which are represented graphically in Fig. 1 (section IV), were as follows:

Temperature.	130°.	140°.	150°.	160°.	170°.	180°.	200°.	220°.	240°.	310°.	448°.
Per cent. insoluble sulphur.....	4.2	5.6	6 7	11.0	18.7	22.5	27.0	29.4	33.0	32.6	34.1

In the above experiments the sulphur entered the bath cold. It was thought that the equilibrium values could be better defined by making another series of experiments in which the sulphur should first be heated for a considerable length of time at a temperature 20° above that of the experiment, so as to create an excess of amorphous sulphur, and be then placed in the bath. At 150° the results were in close correspondence, *viz.*, with cold sulphur 6.7 per cent., with sulphur which had been two hours at 160° previous to being placed in the bath at 150°, 6.8 per cent. At 170°, however, the sulphur which had been two hours at 200° gave 17.4 per cent., while the result with cold sulphur was 18.7. At other temperatures similar discrepancies were encountered.

It will be seen that the above results, taken as a whole, give nothing more than a general idea of the relative proportions of amorphous sulphur obtainable from common sulphur by the use of different temperatures. The values up to 160° also doubtless give a fairly accurate notion of the proportions of S_μ present in solution in the S_λ up to the transition point at which saturation with S_μ occurs.[2] They dispose at once of Berthelot's belief that

[1] Deville, *C. R.*, **26**, 117, gives 34 per cent., which is the exact mean of our results.

[2] Schaum suggested (*Ann.*, **308**, 23) that if the amounts of amorphous sulphur present at various temperatures were known, Van't Hoff's formula, $\frac{d\,ln\,K}{d\,T} = -\frac{q}{RT^2}$, might be

practically no amorphous sulphur exists below 170°. They also render very improbable his conclusion that the amounts of it are constant above 170° and that throughout the lower part of the region 170-448° it constitutes the whole of the material. The divergence from Moitessier's results given in the introduction is doubtless due in part to the sensitiveness of the behavior of sulphur to the influence of traces of impurities, the nature and amount of which must vary in different samples, and in part to the fact that he used very small samples for extraction.

III. AMORPHOUS SULPHUR NOT OBTAINABLE BY SUPERCOOLING WHEN THE SULPHUR DIOXIDE OR SULPHURIC ACID IS REMOVED.

In the earliest experiments made to determine the time required for the production of the maximum yield of insoluble sulphur, although the results were by no means regular, it was observed, especially at the higher temperatures, that there was a distinct falling off from the maximum amounts in the tubes which had been longest heated. It was thought that some action of the air was accountable for this, and the point was reserved for later investigation.

Later it was noticed that freshly recrystallized lots of sulphur gave abnormally small yields, and their use was therefore avoided in the experiments described so far.

When the former idea was tested by passing air through sulphur heated at 448° the yield of insoluble sulphur was found to be as large as usual, no matter how long the stream of air continued. Carbon dioxide, on the other hand, when used simply to displace the air in the tube, reduced the yield below 5 per cent. Its effect was the same when it was allowed to pass through the melted sulphur. Taking all these facts together, it seemed probable therefore that sulphur dioxide or sulphuric acid formed by slow oxidation was in some way responsible for the whole phenomenon of the formation of the amorphous sulphur, and that the removal of the impurity by the use of carbon dioxide, recrystallization, or otherwise, inhibited the production of insoluble sulphur. The

used for the calculation of the heat of formation of the amorphous body. Since Van't Hoff's formula depends on the application of Avogadro's hypothesis to gases or dilute solutions, it could not be expected to give results of any value for a system containing only the two liquid participants in the equilibrium $S_\lambda \rightleftarrows S_\mu$ and no diluent. As a matter of fact the results of the calculation applied to the above data are quite erratic.

following paragraphs give a selection of the experiments which confirmed and enlarged this conclusion.

Sulphuric Acid Present in Sulphur.—When sulphur which has been exposed to the air is washed with water, a small amount of sulphuric acid is easily detected in the washings. This fact is familiar to all chemists[1], and was confirmed by trial in the case of the sulphur employed in these experiments. The quantity varies from 0.0025 per cent. upwards to about 0.02 per cent. When sulphur is heated bubbles of gas appear in it and, according to Frankenheim[2], are reabsorbed when it cools. Malus holds this gas to be sulphur dioxide.

To ascertain the outside limit of the amount of sulphur dioxide contained in amorphous sulphur, a rough quantitative experiment was made. Pure amorphous sulphur was used. Carefully dried carbon dioxide, which was led over heated copper to remove free oxygen, was passed through the sulphur at 150-160°. The issuing gas entered a Liebig bulb apparatus containing bromine water, to absorb any reducing gas. Plugs of glass wool were inserted to retain any particles of free sulphur which might be transported with the gas. The sulphuric acid found in the Liebig apparatus was determined. The amount of amorphous sulphur taken was 62.5 grams. This gave 0.07 gram of sulphur dioxide. As some oxidation of the sulphur by the carbon dioxide undoubtedly occurred, and some sulphur vapor was doubtless carried over, even this small amount is in excess of the amount of sulphur dioxide originally in the amorphous sulphur.

Products of Supercooling when the Sulphur Dioxide is Removed by Prolonged Heating, Heating in Vacuo, Recrystallization, and Washing.—The per cent. of amorphous sulphur after various modes of treatment was as follows:

	Heated 8 hours.	Heated 1½ hours.
At 448°, open tube	2.6	34.0
At 220°, open tube	25.6	29.5
At 220°, 12–15 mm. pressure	11.9	...
At 200°, open tube	25.8	27.0
At 180°, open tube	20.0	22.5

[1] See Norman Leonard: *Analyst*, **26**, 319 (1901); abstract in *J. Chem. Soc.*, **82**, ii, 131 (1902).

[2] *J. prakt. Chem.*, **16**, 12 (1839); Malus, *Ann. Ch. Ph.* (7), **24**, 574 (1901), observed a large volume of gas and noted that after escape of the bubbles and resolidification of the sulphur, heating reproduced an equal amount of fresh gas. This was repeated forty-five times with the same specimen! Surely the air which penetrates the mass after the shrinkage following crystallization and remains entangled when the material is remelted was mistaken by him for freshly formed gas.

At temperatures below 180°, with the open tube, the effect of prolonged heating, if there was any, was too small to be distinguished with certainty.

Sulphur, recrystallized in a fine meal from carbon disulphide, heated for two hours in a steam-bath to free it from the solvent, with no precautions to exclude the air, and then immediately heated for one and a half hours at 448° in an open tube, gave only 10.1 per cent. When precautions were taken to exclude the air, the amount of insoluble sulphur was below 1 per cent.

Recrystallized sulphur which had been exposed to the air for weeks was very finely powdered and washed repeatedly with boiled water to remove the product of oxidation. It was then washed with alcohol and ether, and placed in a steam-bath for thirty minutes, the air having access to it during the *whole* proceedings. After being heated for one and a half hours at 448° in an open tube it gave only 11.3 per cent. of insoluble sulphur.

In all these cases the sulphur was brown and viscous above 160° and yellow and mobile below it, as usual.

The Work of Malus on the Viscosity of Sulphur.—In a paper[1] published in December, 1901, while the present work was in progress, Malus describes a systematic and extensive series of experiments, and shows that the production of viscous sulphur by cooling the heated element rapidly to 100° or to 15° is determined by the presence of sulphur dioxide, and that in the absence of the dioxide the cooled product is mobile at 100° and brittle when solid. The points in his paper with which we are at present concerned are as follows:

"A narrow tube full of sulphur *plunged suddenly* into a bath at 100°, after being heated for *ten* to *fifteen minutes* at 357°, has these properties: (1) reddish yellow tinge, (2) surface highly invaginated, (3) great viscosity, (4) rate of crystallization when inoculated with a monoclinic crystal, two minutes for first centimeter, (5) sudden cooling to 15° gives a soft solid. This liquid he calls S_1. Reheating at any stage gives S_1 again."

"Sulphur *plunged suddenly* into a bath at 100°, after being *three hours* at 357°, has these properties: (1) pale-yellow color, (2) no invagination, (3) mobility, all but a superficial layer 7-8 mm. deep which is viscous (after ten hours at 357° often completely mobile even at surface), (4) rate of crystallization to monoclinic

[1] *Ann. Ch. Ph.* (7), **24**, 491–571.

sulphur five and a quarter seconds for first centimeter, (5) suddenly cooled to 15°, either directly from 357° or after being intermediately at 100°, the product is brittle. This liquid he calls S_2. Reheating at any stage gives S_2 again, and not S_1."

"Sulphur cooled *slowly* to 100°, after being *ten* to *fifteen minutes* at 357°, resembles S_2 excepting that when reheated it gives S_1. He calls this S_2."

"Using 310° (instead of 357°), even with more than twelve hours' heating, the change into S_2 is not always complete."

"At 185°, even 105 hours do not quite suffice to bring the speed of crystallization up to that of S_2."

"At 357° a stream of carbon dioxide for ten to twenty-two minutes, or even the mere insertion of glass rods for five minutes, cause complete transformation into S_2. This effect he explains by supposing that these agents assist in the liberation of the bubbles of gas whose retention gives viscous sulphur (S_1). At 310°, with glass rods, forty minutes are required to give S_2. At 185°, 160 hours are needed. Sulphur dioxide does not produce S_2. On the contrary, when it was passed into S_2, S_1 is formed."

While amorphous or insoluble sulphur is nowhere mentioned in the paper, the interpretation of his results can easily be made out if we make an assumption, for which, however, no basis is to be found in his paper. This assumption is that viscosity and the presence of amorphous sulphur are related to one another as effect and cause. The final result of our own work shows that this assumption is justifiable. The appearance of his paper while our work was in progress in fact brought welcome confirmation of observations which were in some cases difficult to accept.

Since the presence of our S_μ undoubtedly causes the viscidity of sulphur rapidly cooled to 100° or to 15°, it may now be inferred from Malus's paper that heating at 357° for three hours destroys the capacity of the S_μ to be supercooled. At 310° twelve hours, and at 185° 105 hours, are barely sufficient for the same purpose. In each case it is the gradual escape of sulphur dioxide at the surface which permits the change to take place. A stream of carbon dioxide or the presence of glass rods accomplishes the same result by helping the liberation of the gas. Unless the sulphur dioxide is reintroduced the sulphur remains incapable of giving a viscous product containing amorphous sulphur.

Products of Supercooling when Sulphur Dioxide Is Removed or De-

stroyed by Certain Gases and by Alkalies.—As we have seen, the normal amount of amorphous sulphur found after heating at 448° for one and a half hours is 34 per cent. In the following experiments, except where otherwise stated, the same temperature and time were used.

Carbon Dioxide.—Carbon dioxide, washed with water, was passed down to, but not under, the surface of the sulphur. The yield was only 4.5 per cent. When the gas actually passed through the sulphur the yield was the same. A very slight dark deposit was found inside the delivery tube near the exit in all experiments with carbon dioxide. It was probably carbon, produced by a slight reduction by the hot sulphur. Thus, with this gas the presence of sulphur dioxide is not completely excluded.

Nitrogen.—Dry nitrogen gas, passed over heated cupric oxide, and traversing the sulphur, gave only 4.7 per cent.

Ammonia.—When dry ammonia was passed through sulphur at 448° for one hour and a half no amorphous sulphur whatever was found in the product. The action here is doubtless in part chemical, since ammonia interacts with sulphur dioxide. The product had a slight odor of ammonium sulphide.

Hydrogen Sulphide.—Dry hydrogen sulphide passed in the same way gave 0.85 per cent. Here again interaction must occur.

Sulphur Vapor.—Since it appeared that the action of these gases was in large part mechanical, the effect of sulphur vapor itself was tried. Sulphur was boiled vigorously in an open tube for two hours, and, on extraction, was found to contain only 13.2 per cent. of insoluble sulphur. Sulphur vapor was therefore less effective than carbon dioxide or nitrogen.

Alkalies.—A little powdered potassium hydroxide placed in the sulphur at 448° prevented entirely the formation of insoluble sulphur. It is known that sulphur containing the amorphous form, when allowed to stand in an alkaline solution, loses a large proportion of the latter[1]. We found that finely powdered sulphur originally containing 54.7 per cent. of insoluble sulphur, after being allowed to stand in a 5 per cent. solution of sodium carbonate for several days, contained only 8.1 per cent.

Temperatures below 448°.—At temperatures below 448° the effect of gases passing for one and a half hours was observed. The following are a few of the results:

[1] Berthelot: *C. R.*, **44**, 318, 378.

Temp.	Gas.	Per cent. insol. sulphur. Found.	Normal amt. at same temp.
310°	carbon dioxide	6.2	32.5
240°	carbon dioxide	29.[illegible]	33.0
160°	carbon dioxide	11.8	11.0
140°	ammonia	0.0	5.5

It appears that purely mechanical means have no perceptible effect below 180°, but that substances capable of interacting chemically can act at any temperature to destroy the possibility of obtaining insoluble sulphur.

Air at 448°.—Undried air passed through sulphur for two hours gave 34.5 per cent. of insoluble sulphur. Dried air passed for eight and a half hours gave 30.8 per cent. These results are not different from those without air, similar variations having been found when no air was used, but show that the *disappearance* of insoluble sulphur by long heating does not occur when air is employed.

Restoration of the Capacity to Give Insoluble Sulphur by Exposure to the Air and by Use of Sulphur Dioxide.—The capacity once more to yield insoluble sulphur is not recovered by solidification, but it returns gradually during prolonged exposure in a finely powdered condition to the air. One specimen, after treatment with carbon dioxide at 448°, was allowed to solidify and *next day* was heated for two hours at 160°. It gave only 3.2 per cent. (instead of 11). Another, after an hour had been allowed for solidification and loss of all carbon dioxide by diffusion, gave, when once more heated at 448°, only 2.2 per cent. Still another, after solidification, allowed to remain in the tube exposed to the air (but in a compact mass) for twelve days, gave, when heated at 448°, 12.1 per cent. (instead of 34).

A specimen treated with carbon dioxide, and, after solidification, recrystallized from carbon disulphide and quickly freed from the solvent in a steam-bath, gave, when once more heated at 448°, only 1 per cent.

In all cases leading sulphur dioxide through the specimen at 448° for a few minutes completely restored the normal yield of insoluble sulphur. Leading air through the mass for an hour and a half produced the same effect. It thus appeared as if the amorphous body could be produced and destroyed any number of times by the alternate use of suitable substances. The following are a few of the results at 448°:

	Per cent.
1. Dry carbon dioxide	4.5
2. Dry carbon dioxide, then dry air	31.2
3. Dry carbon dioxide, then dry sulphur dioxide	36.5
4. Dry carbon dioxide, then recrystallization	1.0
5. Dry carbon dioxide, then recrystallization, then dry air	32.9
6. Dry carbon dioxide, then dry air, then carbon dioxide	4.9

Best Method of Preparing Sulphur Which Cannot be Supercooled and Yields no Insoluble Sulphur.—It may be inferred from the above experiments that perfectly pure sulphur would give no amorphous sulphur when heated for an hour and a half at 448°. The best way to prepare sulphur closely approaching this ideal is to make it in small quantities, as it is needed, by treatment with ammonia at 448°, recrystallization from pure carbon disulphide to remove traces of ammonium sulphide, and rapid drying in a steam-bath. Sulphur prepared in this way and used at once gives almost no insoluble sulphur, however it may be heated.

The Freezing-Point of Pure Sulphur.—Two samples of the above sulphur were melted without special avoidance of overheating and their freezing-points were determined with the Beckmann thermometer. The freezing-points were 119.170° and 119.165° respectively. Subsequent extraction showed a barely visible quantity of insoluble sulphur. These measurements agree well with the freezing-point of pure sulphur, 119.25°, formerly[1] obtained by extrapolation.

IV. OTHER SUBSTANCES WHICH FAVOR SUPERCOOLING OF S_μ.

Effects of Chlorine, Bromine and Their Hydrides.—All these experiments were made at 448°. The hydrogen chloride and hydrogen bromide were dried and led through the sulphur. For the sake of comparison the chlorine and bromine were *both* carried in a stream of dry carbon dioxide.

Hydrogen Chloride.—This gas increased the yield of insoluble sulphur (38.6 per cent.) and prolonged heating after the stream of gas was stopped and the tube opened to the air did not greatly affect the result (35.4 per cent.). One experiment was made to ascertain whether, when *the cooling is slow* the adjustment to a condition of equilibrium, which causes the insoluble sulphur to disappear, is disturbed by hydrogen chloride. Only 0.8 per cent. of insoluble sulphur was found.

Hydrogen Bromide at 448°.—This gas gave 34.9 per cent.

[1] *Z. physik. Chem.*, **42**, 476.

Chlorine at 448°.—Dry chlorine gas gave 56.8 per cent. The product was comparatively liquid and sticky, without any elasticity, and took many days to become hard.

Bromine at 448°.—As it seemed likely that the large yield in the case of chlorine had been caused partly by interaction between a chloride of sulphur and the water used in cooling, the material in this case was cooled by pouring over the bottom of a dry metal pail standing in a freezing-mixture. Part of the product was ground in a mortar with chloroform to remove any bromide of sulphur, which by interaction with the moisture from the air might have added to the yield of insoluble sulphur, and was then extracted. It gave 38.22 per cent. A good deal of insoluble sulphur had remained unhardened and ran in droplets through the thimble used in the extraction and was lost. The rest of the product was treated with chloroform, and then freed from this solvent and ground up with carbon disulphide. When this had evaporated the product was pulverized and extracted. The yield in this way was 65.1 per cent.

Another portion was cooled slowly. If the presence of a bromide of sulphur had contributed to the above large yield the same influence would have been noticed, probably on a more extensive scale, in a slowly cooled specimen. The product, which was brittle when cold, was rubbed with chloroform and was afterwards extracted in the ordinary way. The yield was 1.1 per cent, so that the large yield above was independent of any action of moisture on a bromide of sulphur.

Restoration of the Capacity to Give Insoluble Sulphur by Hydrogen Chloride, Sulphuric Acid and Phosphoric Acid.—It was naturally anticipated that the above substances would also restore the capacity to give insoluble sulphur, and it was found that they did so. Even dried finely powdered metaphosphoric acid, when introduced in small amount, had the same effect. In this case subsequent treatment with carbon dioxide did not once more destroy the capacity to give insoluble sulphur, the phosphoric acid being non-volatile. The following are typical experiments, all made at 448°:

	Per cent.
Hydrogen sulphide, then dry hydrogen chloride	43.3
Carbon dioxide, then metaphosphoric acid	31.0
Carbon dioxide, then hydrogen chloride	44.3

In the last two experiments special care was taken to purify the carbon dioxide from free oxygen by passage over heated copper. These two experiments in particular show conclusively that the normal amount of insoluble sulphur can be formed when sulphur dioxide is almost absolutely excluded. The amorphous sulphur can therefore hardly be a chemical compound of sulphur with sulphur dioxide, since it can equally well be formed by the help of other bodies like metaphosphoric acid and hydrogen chloride.

That the restoration occurs also at lower temperatures was determined by experiment. Thus one specimen of sulphur was kept at 140° and treated first with ammonia to remove the capacity to give insoluble sulphur, and then with a few drops of concentrated sulphuric acid. Thorough mixing was secured by continuous use of a stirring apparatus. The amount of insoluble sulphur was 5.30 per cent., the proportion given by ordinary sulphur at this temperature.

In another experiment made in the same way at 140°, with continuous stirring, an effort was made to determine also the time required for the restoration. Sulphuric acid and powdered metaphosphoric acid were compared, the vessels being present simultaneously in the same bath. Samples were taken out of each and chilled and extracted separately. It was found, however, that in both cases the first sample, taken after ten minutes, gave as much insoluble sulphur as the later ones. The maximum amount with the former agent was 5.77 per cent. and with the latter 5.79 per cent. This reaction speed, which is shown by preliminary experiments[1] to be much greater than that proper to ordinary sulphur, was especially surprising when the general inactivity of phosphoric acid and its vanishingly small solubility in melted sulphur were considered.

Effects of Iodine; Preliminary Experiments.—Since iodine had been found by Dietzenbacher[2] to confer unusually persistent plasticity upon supercooled sulphur it was expected that by its use larger amounts of insoluble sulphur would be obtained. Powdered iodine dissolves rapidly and in large amounts in melted sulphur. The solution is deep reddish brown in color. Except where otherwise stated, we used two parts of iodine to one hundred of sulphur. These solutions gave off a little iodine vapor, but the loss of iodine

[1] Not yet published.
[2] *C. R.*, **56**, 39 (1863).

was inconsiderable, even during one to two hours at the higher temperatures.

It was determined that rubbing the chilled, viscous mass immediately with carbon disulphide, allowing the solvent to evaporate, pulverizing the residue and leaving it for two days to solidify completely gave somewhat larger yields of insoluble sulphur when iodine was present than did the method used in earlier experiments. This modification of the former method[1] was therefore here substituted for the mere spontaneous hardening. It had the additional advantage that nearly all the iodine evaporated with the carbon disulphide and the powdered sulphur was but slightly colored by a trace of iodine remaining.

As the yields of insoluble sulphur were uniformly larger than with any other substance except bromine, it was thought, as before, that this might be due to interaction between an iodide of sulphur and the water used for cooling. Berthelot states[2] that the chloride and bromide of sulphur give larger proportions of insoluble sulphur by the action of water than any other mode of precipitation. It was found, however, that none of the amorphous sulphur was due to this cause. The so-called "iodide of sulphur" was prepared by Guthrie's method[3] and used as if it had been a supercooled mass. After treatment exactly like that used in the regular experiments the residue was extracted. It gave no insoluble sulphur. This conclusion was confirmed in another way. Sulphur was heated with 2 per cent. of iodine at 448° for one and a half hours and was then allowed to cool slowly in the large iron tube. While the insoluble sulphur thus had an opportunity to disappear in the usual manner any iodide of sulphur which might be present or might be formed during the cooling was bound to remain. Treatment of the residue in the usual manner, however, did not yield even a trace of insoluble sulphur. Preliminary experiments having shown that all results with iodine were much more regular and consistent than with sulphur dioxide, a more extensive and systematic series of experiments was made with this substance.

[1] In the work described in sections II and III this modification made no difference in the yield and most of the experiments in which it was used have therefore been omitted (see, however, section V).

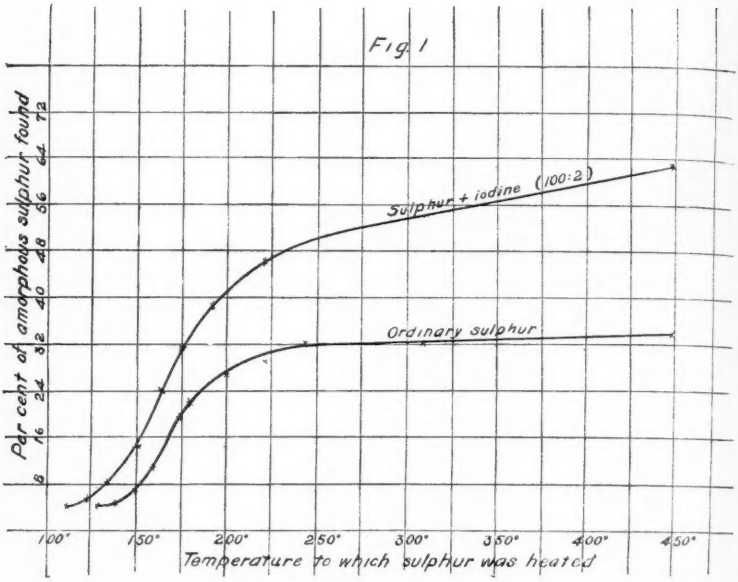
[2] *Ann. Ch. Ph.* (3), **49**, 482.

[3] McIvor, *Chem. News*, **84**, 5 (1902), finds the so-called moniodide to be a solid solution and not a compound. The fact that it gave no amorphous sulphur by the above treatment seems to support this view. Boulough, *C. R.*, **136**, 1577, finds that sulphur and iodine give a eutectic mixture melting at 65.5° and no compound.

The Results with Two Parts of Iodine to One Hundred of Sulphur.—At the temperatures from 120° to 310° (see following table) two tubes previously held for two hours at a temperature from 10-15° higher were placed in the same bath with two cold tubes and the four were kept at the temperature of the bath (column 1) for two hours. At 110° two tubes previously kept at 125° alone were used, as this preliminary superheating was necessary to melt the sulphur. At 448°, on the other hand, the equilibrium point was reached from below only, as a higher temperature than 448° could not be obtained without the use of more than atmospheric pressure. In the following table the numbers in the second and third columns are the means of the four results of extraction (two samples of the content of each of two tubes). The individual results did not in any case differ from the mean by more than 2 per cent. of the amount of the insoluble body. As will be seen, the proportions of amorphous sulphur formed with rising and with falling temperature correspond more closely than did the results of experiments without iodine.

	Per cent. insoluble sulphur.		
Temperature.	Equilibrium from below.	Equilibrium from above.	Mean.
110°	.....	4.05	4.0
120°	5.33	5.35	5.3
135°	8.60	8.61	8.6
150°	13.44	14.14	13.8
165°	23.76	24.51	24.1
175°	31.59	31.50	31.5
190°	37.81	38.21	38.0
220°	46.73	47.26	47.0
310°	53.70	54.61	54.2
448°	62.64	.....	62.7

In Fig. 1 these results are exhibited graphically (temperature horizontally and per cent. of insoluble sulphur vertically), together with the results in the absence of iodine (section II). The latter, on the lower curve, are uniformly much smaller. The lowness of the amount at 310° on the upper curve is due to the fact that, while at 448° the tube on immersion in ice and water bursts violently and a minute dispersion and complete cooling of the sulphur is instantly produced, at 310° the temperature is not high enough to bring about this result and intimate and immediate contact is more difficult to secure. At lower temperatures the reversion of the insoluble sulphur is less rapid and therefore the effect of slower contact with the ice must be less conspicuous.



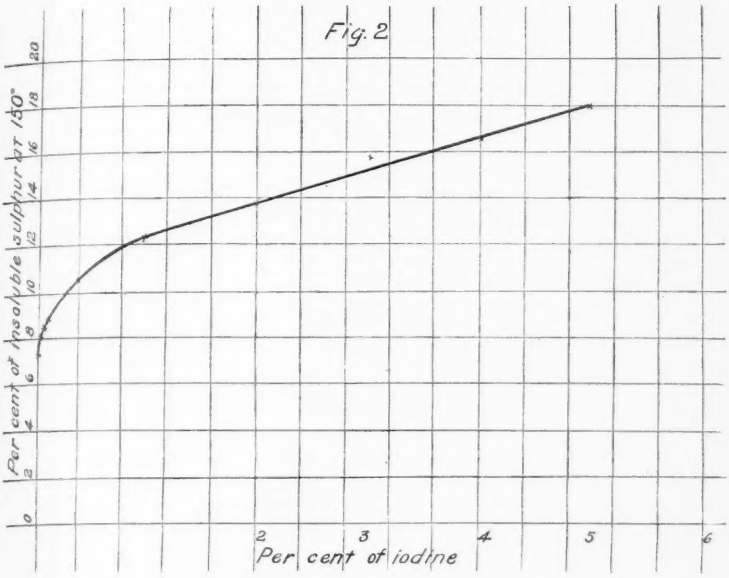
Results with Varying Proportions of Iodine at 150°.—The following table shows the marked effect which increasing amounts of iodine produce at the same temperature. All the experiments were done simultaneously in the same bath. Twenty-five grams of sulphur were used in each of them, as in each of the preceding experiments. The quantities of iodine are parts with one hundred of sulphur.

Iodine.	0.	0.01.	0.04.	0.1.	0.4.	1.	2.	3.	4.	5.
Per cent. insoluble sulphur.....	6.7	8.16	8.38	8.90	10.52	12.26	13.79	15.85	16.47	17.86

The graphic representation of these results (Fig. 2), in which the quantity of iodine is plotted horizontally and that of insoluble sulphur vertically, seems to show that from 1 part of iodine onwards the increase in the amount of insoluble sulphur is approximately proportional to the amount of iodine.

V. OTHER METHODS OF SUPERCOOLING AND OF TREATING THE SUPERCOOLED MASS.

Another Method of Treating the Supercooled Product.—In view of Berthelot's statement above quoted, an attempt was made to ascertain the effect on the yield of various modifications in the



treatment. Since the sticky amorphous sulphur is freely dissolved by carbon disulphide, but may be largely recovered in insoluble form by evaporation[1], it seemed probable that a preliminary rubbing in a mortar with the solvent and removal of the latter by evaporation would forestall considerable reversion to the soluble form. To test this question together with that of the effect of varying lengths of time for solidification, a large quantity of sulphur was heated at 448° for two hours, and then poured into ice in a thin stream. The product was divided into six portions, with the following treatment and results:

	Per cent. insoluble sulphur.
1. Extracted ordinary way after two days	36.6
2. Extracted ordinary way after six days	36.1
3. Treated by evaporation at once and pulverized and extracted immediately	30.8
4. Treated by evaporation at once and pulverized and extracted three days later	32.3
5. Treated by evaporation after two days and then pulverized and extracted	27.8
6. Treated by evaporation after six days and then pulverized and extracted	35.9

[1] *Cf.* Berthelot: *Ann. Ch. Ph.* [3], **49**, 476.

The results show that with common sulphur our regular method of allowing several days for solidification and then pulverizing and extracting give the largest yield.

Supercooling by Quenching Burning Sulphur.—More sudden cooling can be achieved by distilling the sulphur in a fine, burning stream from a retort (placed 50 cm. above a vessel of ice and water). In this way the sulphur is kept near to its boiling-point until it actually enters the water in a rapid succession of beads. In the set of experiments made in this way a test was also made of the influence of acids on the cooled product.

	Per cent.
1. Soft beads extracted at once (uncorr.)	58.8
2. Soft beads treated by evaporation, pulverized and extracted at once	51.3
3. Product after six days pulverized and extracted	40.0
4. Soft beads seven days under strong nitric acid, pulverized and extracted	30.6
5. Soft beads six days under strong sulphuric acid, pulverized and extracted	33.2
6. Distilled with 2 per cent. iodine, treated by evaporation, pulverized and extracted after one day	52.1

Another single experiment similar to 2:

2_1. Soft beads treated by evaporation, pulverized and extracted at once	51.1

No. 1 has no claim to trustworthiness, as the beads ran together in the extractor and the carbon disulphide did not reach the inner part of the material. On the other hand, some liquid insoluble sulphur formed an emulsion with the solvent and was lost. No. 3 corresponds to No. 2 of last set, and shows an increased yield by the new method of chilling. No. 2 corresponds to No. 3 of last set and shows a greatly increased yield by combined use of the new methods of chilling and treating the supercooled mass. The long stream of sulphur was heated in an atmosphere of sulphur dioxide produced by the combustion, and the soft beads were saturated with the same substance and therefore were perhaps still subject to its influence after they were cold. Apparently, under these circumstances the treatment of the chilled mass by rubbing with carbon disulphide does markedly increase the yield. The chilling of a burning stream raises the yield from 34 per cent. to 40 per cent. (No. 3) and the evaporation process adds 11 per cent. more (Nos. 2 and 2_1). In No. 6 the combined influence of iodine and distillation was tried. In this case it was found that the small

amount of iodine remaining in the material after it had been treated by evaporation and pulverized caused a gradual increase in the yield of insoluble sulphur. Another portion of the material from No. 6 was extracted three days later and gave 52.1 per cent., while a third portion extracted thirteen days later still contained 52.6 per cent. This effect is interesting in connection with the retardation of the rate of hardening which Kastle and Kelley[1] observed when plastic sulphur was kept under decinormal iodine solution. Contrary to Berthelot's statement[2] we found in the above and other experiments that keeping the soft product under acids gave no greater yields than other ways of treating the same material. A much finer condition of subdivision, such as that secured by precipitation, is necessary in order that the acid may be effective.

Supercooling by Means of Ether.—Finally, cooling with ether, which in Berthelot's hands gave the largest yields, was tried. The sulphur was boiled in a tube drawn out to a capillary at the bottom. By breaking this capillary and applying pressure on the surface of the sulphur by means of a foot-blower, the material was rapidly forced out in a fine jet into a vessel of ether surrounded by ice and salt and situated at the bottom of a pail filled with carbon dioxide gas to prevent accidental inflammation. The sulphur formed minute beads and could not well have been chilled more suddenly. The product was treated by evaporation with carbon disulphide and pulverized and extracted at once. It gave 44.4 per cent. insoluble sulphur. While the yield was in excess of the largest obtained from ordinary sulphur by cooling with ice, it is considerably smaller than that given by the distillation experiments in which perhaps the liberal supply of sulphur dioxide is the determining cause of the difference. Berthelot's 85 per cent. was from a distillation experiment, in which sulphur dioxide intervened, and he extracted the soft material at once. This experiment has been criticized already.

[1] *Am. Chem. J.*, **32**, 489.

[2] *Ann. Ch. Ph.* [3], **49**, 484.

VI. COMPARISON OF THE BOILING-POINTS AND SPECIFIC GRAVITIES OF SPECIMENS OF SULPHUR WHICH RESPECTIVELY DO AND DO NOT YIELD INSOLUBLE SULPHUR, WITH A VIEW TO ASCERTAINING WHETHER THESE TWO KINDS OF SULPHUR ARE ACTUALLY OF THE SAME OR OF DIFFERENT CONSTITUTION NEAR THE BOILING-POINT.

The fact that insoluble sulphur lowers the freezing-point of melted sulphur shows definitely that insoluble sulphur comes from the solidification of a modification of sulphur which is distinct from soluble sulphur and can exist in solution in melted sulphur, at all events near to its temperature of solidification. The experiments described thus far in this paper *seemed* to show that this distinct modification could be destroyed and reproduced at will. It was inadmissible to suppose that the gases which appeared to effect its removal and reproduction acted simply as catalytic agents. Such agents may affect the speed of an action, but cannot afterwards alter the proportion natural to a state of equilibrium.[1] The subsequent withdrawal of a mere catalytic agent does not diminish the amount of the product, as seems here to be the case when the sulphur dioxide is driven out. At all events these statements apply strictly in all cases where the introduction of the catalytic agent and its withdrawal are not accompanied by the performance of any work. In the present instance it is impossible that, by the introduction of gases or mere glass rods, work could have been done in amount even remotely approaching that required to accomplish such extensive displacements of the equilibrium point. On the other hand, the hypothesis that amorphous sulphur is a compound of soluble sulphur with some other substance or substances is equally difficult to accept. The molecular proportion of sulphur dioxide is very minute and other bodies may take its place, giving the same product. The idea that the insoluble modification could be really altered in amount by foreign bodies was therefore given up.

The alternative view is that once the maximum amount at a given temperature has been reached, the proportion of the insoluble modification is not affected by leading gases, for example ammonia and sulphur dioxide, alternately through the mixture. The explanation of the appearance or non-appearance of insoluble sulphur would then have to be sought in some influence

[1] Ostwald: *Handbuch*, **2**, 2, 262.

which the foreign body exerted at some stage of the operation of cooling. An attempt to test this alternative was made at the boiling-point and at two temperatures somewhat below 448°. It is a question of determining whether two liquids, one of which does and the other does not *give* at least 34 per cent. of a distinct substance, differ as markedly in physical behavior as two such liquids would do if only one of them *actually contained* this amount of a foreign material. The boiling-points and specific gravities were the properties which could be most easily compared. A rough calculation showed that 30 per cent. of a non-volatile body of molecular weight equal to that shown by the freezing experiments to be proper to dissolved amorphous sulphur (S_∞), should have elevated the boiling-point by an amount of the order of 10°-20°. Unless insoluble sulphur had exactly the same vapor pressure as soluble sulphur at 448° some difference in the boiling-points should have been observable, provided always the specimens compared were not identical in constitution. Even if the vapor-pressures happened to be identical at 448°, they would not be so also in a partial vacuum at 406°. The actual comparison described below showed that, both at atmospheric pressure and under somewhat reduced pressure, the boiling-points were identical, and that at 448° and at 302.5° the specific gravities were alike.

These facts, together with others detailed in the preceding paper, led therefore to the conclusion that the gases and other substances affected the sulphur during the process of cooling only, and at some temperature considerably below the boiling-point.

The Boiling-point of Sulphur and Its Relation to Insoluble Sulphur.—A quantity of recrystallized and redistilled sulphur was placed in a wide tube, surrounded by asbestos cloth to reduce the loss of heat by radiation and convection. The bulb of a thermometer, filled with nitrogen under pressure and graduated up to 550°, was immersed in the boiling material. After half an hour the reading became steady at 437.2°. Sulphur dioxide was then passed in slowly for three hours, during which the reading did not change. Then dry carbon dioxide was led into the sulphur for one hour without any alternation in the boiling-point of as much as 0.1° being observed. Then ammonia was used for an hour and the reading remained exactly 437.2°. That the instrument was in working order was shown by the fact that when a more rapid stream of one of the gases was allowed to enter, the bubbles of the

cold gas striking the bulb of the thermometer immediately produced a slight fall in the reading. But the original temperature was recovered as soon as the speed of the gas was diminished.

Under somewhat reduced pressure the constancy of the boiling-point could not be maintained so perfectly, even while no gas was being introduced. The readings, at intervals of three to ten minutes, were as follows, the symbol interposed indicating that ammonia or sulphur dioxide was introduced at that point: 405.6°, 405.6°, 405.7°, (NH_3), 405.8°, 406.0°, 405.7°, 405.7°, (SO_2), 405.7°, 405.8°, 405.9°, (NH_3), 405.9°, 405.9°, (SO_2), 406.0°, 405.9°, (Se), 407.2°, 407.2°, 407.0°.

To show that actual presence of a foreign solute *did* elevate the boiling-point, 1.025 grams of selenium[1] was added at the point indicated. This produced an immediate elevation of 1.2°. The weight of sulphur used was about 81 grams.

The Specific Gravity of Liquid Sulphur and Its Relation to Insoluble Sulphur.—The specific gravity of liquid sulphur was determined with the utmost care at the temperature of diphenylamine vapor and at that of sulphur vapor. Sulphur which had been recrystallized and twice distilled was employed. At each temperature two measurements were made, one with the sulphur in its natural condition, the other with sulphur through which ammonia had been passed. Glass bulbs, with short exit tubes, holding 15-20 cc. were used as pycnometers. They were completely filled with the liquid sulphur, and the expansion when they were lowered into the bath caused the excess of sulphur to overflow. The volumes of the bulbs and the coefficient of expansion of the glass were determined by calibration with mercury between 0° and 100°. The results were as follows, the first column (I) under each temperature giving the data for the specimen of natural sulphur, and the second (II) those for sulphur treated with ammonia.

	Diphenylamine vapor: 302.5°.		Sulphur vapor: (448° ?).	
	I.	II.	I.	II.
Weight of mercury filling pycnometer at 0°, in grams	228.868	267.850	267.850	267.850
Volume at 0°, in cubic centimeters	16.835	19.701	19.701	19.701
Volume corrected to temperature	16.982	19.874	19.957	19.957
Weight of sulphur	28.876	33.742	31.981	31.916
Specific gravity of sulphur	*1.697*	*1.697*	*1.602*	*1.593*

[1] From the heat of vaporization of sulphur at 448°, namely 362, a rough estimate of the molecular weight of selenium in solution in sulphur may be made from the above data. The value corresponds to the formula $Se_{3.4}$.

Coefficient of expansion of the glass, 0.000029.

Specific gravity of mercury at 0°, 13.5956.

The substantial agreement of the pairs of specific gravities, as well as of the pairs of boiling-points, seem to justify the conclusion that there was no difference in constitution at 300-448° between sulphur which did and sulphur which did not give insoluble sulphur.

VII. COMPARISON OF THE SOLUBILITIES OF SULPHUR WHICH DOES AND SULPHUR WHICH DOES NOT GIVE INSOLUBLE SULPHUR, WITH A VIEW TO ASCERTAINING WHETHER THESE TWO KINDS OF SULPHUR ARE ACTUALLY OF THE SAME OR OF DIFFERENT CONSTITUTIONS BETWEEN 119.25 AND 160°.

The results of the experiments on the boiling-point and specific gravity showed that in the region between the transition point (160°) and the boiling-point the amorphous sulphur was present in solution in sulphur whether it could be obtained by sudden cooling or not. It remained to ascertain whether amorphous sulphur was similarly present under all circumstances in liquid sulphur below 160°. Since below 160° amorphous sulphur is the less stable form it should be more soluble than melted crystalline sulphur. If, therefore, sulphur which has been treated with ammonia really contains no amorphous sulphur, while that which has been treated with sulphur dioxide does contain from 4 to 12 per cent. of the less stable modification, there should be a difference in the solubilities of the two kinds in a substance like triphenylmethane. Moreover, the difference in solubility observable should be exaggerated by the fact that the solution of the amorphous sulphur will displace the equilibrium by which it is related to the soluble material and so lead to the continual restoration of its natural concentration in the sulphur phase until the organic solvent is saturated with it.

This question was put to the test by preparing solutions containing known concentrations of sulphur and triphenylmethane. Ammonia and sulphur dioxide were led through the solutions for thirty to sixty minutes, and after the treatment with each gas the temperatures at which the solutions became cloudy through separation of sulphur were determined repeatedly. Constant temperatures of saturation were easily found. The results were as follows:

Amount of S with 10 grams $CH(C_6H_5)_3$.	Temperature of saturation.	
	After SO_2.	After NH_3.
11.43	138.5	138.3
15.71	143.0	143.0

These points lie close to the curve given in the preceding paper[1] and there was no difference between the solubilities of the two kinds of melted sulphur. From this it may be inferred that the sulphur phases which separated contained identical proportions of dissolved amorphous sulphur. Of course when the solutions were suddenly cooled, only those containing free sulphur dioxide showed any amorphous sulphur in the hardened product. With the others this product was brittle and crystalline from the first, the amorphous sulphur having reverted to the soluble form during the chilling.

VIII. DISCUSSION OF THE RESULTS.

All Specimens of Sulphur Have the Same Constitution at Identical Temperatures when They Have Reached a Condition of Equilibrium.—The experiments described in section VI show that specimens of sulphur which, respectively, do and do not give insoluble sulphur are identical in constitution when they have reached a state of equilibrium at temperatures near to the boiling-point. These specimens all contain the same proportion of the liquid which, when supercooled, gives amorphous sulphur. Again, the absence of any displacement of the transition point at 160° (see preceding paper, "On Amorphous Sulphur, II," sections II, III and V) leads to the same conclusion for all specimens of sulphur which are in a condition of equilibrium at that point. Similarly the experiments described in section VII of this paper lead to this conclusion for different specimens of liquid sulphur throughout the range of temperatures between the freezing-point and the transition-point (119.25- to 160°.)

It is only at the freezing-point itself, when liquid sulphur passes into solid, monoclinic sulphur, that a difference seems to assert itself. The first paper of this series shows that the liquid from which insoluble sulphur can be obtained by chilling freezes at various temperatures, all below 119°. The experiments in section IV of this paper, on the freezing-point of pure sulphur, show that specimens which give no insoluble sulphur freeze close to 119.25°. This difference between specimens which do and do not give insoluble sulphur is only apparent, however. It must be remembered that the specimens employed in the determination of freezing-points in the work of the first paper were not in a condition of equilibrium. They were obtained purposely by rapid cooling from higher tem-

[1] *Loc. cit.*

peratures. The longer they were kept before being placed in the freezing apparatus the more nearly they approached in freezing-point the samples treated with ammonia of which use was made in this paper.

Thus the study of liquid sulphur stage by stage from the boiling-point to the freezing-point shows conclusively that all specimens of sulphur, when they have reached a condition of equilibrium at identical temperatures, have the same constitution. It shows that, whether when chilled they give insoluble sulphur or not, they all contain definite proportions of the form which, if it can be supercooled, yields insoluble sulphur. It shows that the proportion of amorphous sulphur depends only on the temperature.

The Nature of Amorphous Sulphur.—At the freezing-point amorphous sulphur is clearly a third variety and not one of the two, namely, solid-monoclinic and melted-soluble sulphur (S_λ), which are directly concerned in the transition. This is clear, because when present it displaces this transition point. It is equally evident that amorphous sulphur is not a third variety, but is itself one of the two liquids, namely, S_λ and S_μ, whose transformation constitutes the transition at 160°. This is evident because its presence does not displace this transition point. The conclusion is therefore reached that amorphous sulphur is supercooled S_μ.

The fact that it is amorphous, and must therefore be a supercooled liquid of some kind, is in harmony with this conclusion. That 100 per cent. of S_μ cannot be secured in the hardened condition is evidently due to partial reversion to the soluble form in the plastic mass. We have shown that when proper conditions are realized, as during precipitation, this reversion may be entirely prevented.

In view of the above conclusion it is clear that even minute traces of foreign bodies influence strongly the capacity of S_μ to become supercooled. They evidently exercise this influence during the chilling process. Apparently those which, like ammonia and hydrogen sulphide, cause the production of no insoluble sulphur do so only by destroying the sulphur dioxide which would otherwise have the opposite effect. This is evident because recrystallization and immediate use give the same result as leading in ammonia, and inability to be supercooled is therefore a property

of pure S_μ. Sulphur dioxide and iodine, on the other hand, favor in some way the supercooling of S_μ.

At What Stage and in What Way Do Foreign Bodies Influence the Supercooling of S_μ?—At least three answers to these questions are possible.

(1) The foreign body may retard the backward progress of the action $S_\lambda \rightleftarrows S_\mu$ (possibly, but not very probably, by destroying something which if present alone would hasten it) and so diminish the speed with which the chemical equilibrium adjusts itself in response to the rapid changes in temperature attending the operation of chilling. This sort of influence, if exerted at all, will be exerted throughout the whole range of temperatures and stages from the boiling-point until hardening is complete.

(2) The foreign body may play no part until the transition from the liquid to the hardened condition is in progress, and at that time may determine the formation of the insoluble sulphur.

(3) The foreign body may exert its influence at the transition point from S_μ to S_λ (160°), favoring perhaps the supersaturation of S_μ with S_λ, or hindering the initiation of the new phase of which S_λ is the chief constituent. A fact which repeatedly forced itself upon our attention in the work described in the preceding paper shows that this supposition touches closely what is probably the true explanation of the greater part of the influence of foreign bodies. We have seen that distilled sulphur does not show the absorption of heat or the onset of viscosity so sharply as do the other kinds. Apparently the formation of the new phase which marks the upward transition does not so readily take place with sulphur prepared under the conditions attending distillation. It may, therefore, be presumed that the inverse change from S_μ to S_λ brought about by cooling will be similarly less prompt with distilled sulphur. Now it has been shown by Berthelot[1] and by ourselves (section V) that, when no foreign ingredient has been purposely introduced, this kind of sulphur is precisely the one which gives by chilling the largest yields of insoluble sulphur.

There are probably still other possible modes in which the results may be brought about, and, in any case, it is not likely that any one kind of influence operates alone. Thus, in section V the influence of iodine in continuing to increase the proportion of insoluble sulphur after hardening is complete has been demonstrated.

[1] *Ann. Ch. Ph.* [3], **49**, 482.

Yet if (2) were the sole cause it would be difficult to see why previous heating at various different temperatures should give different proportions of insoluble sulphur.

A considerable amount of experimental work along the lines just indicated, as well as in other directions which there has been no occasion to mention in these papers, has already been done. It is hoped that a part of this will be sufficiently advanced for publication within a short time.

Analogy in the Behavior of Iron and Steel.—In conclusion it may be pointed out that the problems raised in this work are of especial interest in view of their similarity to those encountered in the study of the chilling of iron and steel. The similarity may be indicated by two examples taken from an almost endless number that might be used. Pure iron (α-ferrite) passes into β-ferrite at 765° and into γ-ferrite above 890°. In this last condition it is non-magnetic. These temperatures are transition points similar to 95.6° and 160° for sulphur, save that in the case of iron both lie within the region in which the material is solid. When chilled, γ-ferrite promptly reverts to α-ferrite and recovers its magnetic qualities. The addition of 12 per cent. of manganese, however, so reduces the facility with which γ-ferrite passes into β- and α-ferrite that when the alloy is chilled the product contains only supercooled γ-ferrite and is wholly non-magnetic. Even when cooled very slowly or when kept for hours at 400-500° the specimen passes with difficulty into a condition of equilibrium by changing into an alloy of manganese with α-ferrite. This is an example of a foreign body hindering a transition which involves the production of a new phase. Again, Charpy and Grenet[1] have shown that silicon favors the separation of graphite in cast iron, facilitating the initial appearance of the carbon phase and causing the separation to proceed more rapidly after it has been initiated, while at the same time affecting in no way the amount finally deposited when the system has reached a condition of equilibrium. Here a foreign body seems to assist a process involving the production of a new phase. Our view is that the phenomena of supercooling shown by sulphur and by iron are to be explained on the same principles.

RESULTS OF THIS INVESTIGATION.

(1) The hardening of plastic sulphur is discussed and it is shown

[1] *C. R.*, **134**, 103.

that partial reversion to soluble sulphur prevents the securing in quasi-solid form of the whole of the amorphous sulphur present. It is stated, however, that sulphur formed by precipitation in presence of concentrated acids does yield 100 per cent. of insoluble sulphur and that only the impossibility of realizing the requisite condition of very fine subdivision is, therefore, responsible for the smaller yields from melted sulphur which has reached the highest temperatures previous to being chilled.

(2) A new series of measurements of the proportions of insoluble sulphur formed when common sulphur is chilled from various temperatures is given. The amounts vary from 4.2 per cent. at 130° to 34 per cent. at 448°. In this and all other cases described, only the insoluble sulphur which remains after the viscous material has completely hardened is estimated.

(3) It is shown that when sulphur is subjected to prolonged heating at 448°, or is heated for a shorter time *in vacuo*, or is used immediately after recrystallization, or is washed with water before being heated, the amount of insoluble sulphur obtainable by chilling is greatly reduced. The effect of these modes of treatment seems to be to remove a trace of sulphuric acid which sulphur acquires by exposure to the air.

(4) It appears that gases like carbon dioxide and, particularly, ammonia and hydrogen sulphide, when led through melted sulphur destroy the ability to give insoluble sulphur. Their use does not, however, affect the viscosity above 160°.

(5) It is shown that air and sulphur dioxide restore the ability to give insoluble sulphur. The halogens, the halogen hydrides, and even phosphoric acid have the same effect.

(6) It is found that sulphur which has been treated with ammonia while melted and has afterwards been recrystallized, if used at once, freezes at 119.17° and contains no insoluble sulphur.

(7) Sulphur containing iodine (100 : 2) gives, when heated and chilled, large amounts of insoluble sulphur. These range from 4 per cent. at 110° to 62.7 per cent. at 448°.

(8) The increase in the amount of insoluble sulphur obtained at 150° is approximately proportional to the quantity of iodine present when the quantity of the latter is 1 per cent. or more.

(9) Sulphur prepared by distilling the element and quenching the burning stream in ice water gives 51 per cent. of insoluble

sulphur. Chilling boiling sulphur in ether gives 44.1 per cent. of the insoluble form.

(10) It is shown by identity in boiling-points under ordinary and reduced pressures and identity in specific gravities that sulphur which will give the insoluble form when chilled is identical in constitution near the boiling-point with that which will not.

(11) It is shown by identity in solubility between 120° and 160° that the two kinds of sulphur mentioned in (10) are identical in constitution also below the transition point of S_μ to S_λ (160)°.

(12) The facts referred to in (10) and (11), together with the conclusions of the preceding paper showing the identity of the two kinds of sulphur at the transition point (160°) itself, demonstrate that the insoluble form is present in all specimens of melted sulphur in proportions depending upon the temperature alone, whether by treatment with ammonia or otherwise they have lost the capacity to give insoluble sulphur by chilling or not.

(13) The conclusion is reached that amorphous sulphur is supercooled S_μ—the form stable above 160°.

(14) With pure sulphur, freed from sulphur dioxide by recrystallization or by treatment with carbon dioxide above 310°, or by treatment with ammonia or hydrogen sulphide at any temperature at which it is fluid, the S_μ reverts so rapidly to the soluble form that it cannot be supercooled. When traces of sulphur dioxide, iodine and other substances are present, S_μ is more or less completely supercooled and gives amorphous sulphur. The way in which the latter class of foreign substances produces this effect is still being investigated.

(15) The close analogy of these phenomena to those observed in the cooling of cast iron and steel is pointed out.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF ORGANIC SUBSTANCES CONTAINING OXYGEN WITH NITRIC, SULPHURIC AND CHLORSULPHONIC ACIDS.

By D. McIntosh.

Received June 14, 1905.

The basic properties of organic compounds containing oxygen have been discussed in a number of articles,[1] and the quadrivalence

[1] *J. Chem. Soc.* (London), **85**, 919 (1904); **85**, 1098 (1904).

of the oxygen atom has been advanced as an explanation of the constitutions of the compounds formed. In all cases previously investigated the compounds had low melting-points, above which temperatures decomposition took place, with the formation of substituted products. Cohen and Gatecliff[1] have lately described additive compounds of the ethers with nitric acid, obtained, however, only as liquids, which were prepared at relatively high temperature. The existence, at such temperatures, of compounds in which the oxygen functioned as a tetrad, seemed so unlikely that I have made some experiments on the additive compounds of nitric acid with ether, alcohol, and acetone, and at the same time have endeavored to obtain compounds with a di-basic acid (sulphuric) and with chlorsulphonic acid.

The organic substances were purified by the usual method; to prepare the nitric acid, a mixture of nitric and sulphuric acids was distilled under reduced pressure, as described by Velley and Manley;[2] it contained probably 99.8 per cent. of acid.

Experiments with nitric acid.—The compounds were prepared by slowly adding the acid at —50° to the organic liquid cooled to —80°. The amount of heat evolved was small compared with that given out during the formation of similar compounds with the hydrogen halide, but larger than if addition compounds[3] with the halogen were formed. A white compound soon makes its appearance on the addition of acid to ethyl ether. It melts at —25°, and at a little higher temperature oxidation begins. At room temperature the action is violent, so that the bodies investigated by Cohen and Gatecliff must have contained water; and the agreement with the formulae given, in the case of the ethyl ether at least, must have been accidental.

A great many analyses of the ether-nitric acid compound were made, but with unsatisfactory results. For each molecule of ether the analyses showed between one and two molecules of acid present. It is possible that the compound is $C_4H_{10}O,2HNO_3$ and that it is contaminated by various products formed by oxidation of the ether.

More definite results were obtained with ethyl alcohol and with acetone. The former gave a white crystalline compound melting at —30°. This product contained 53.8, 53.9, 53.9 per cent. HNO_3,

[1] *Chem. News*, **90**, 265 (1904).
[2] *Trans. Royal Soc.*, **A191**, 363 (1898).
[3] *J. Chem. Soc.* (London), **87**, 784 (1905).

while in C_2H_6O,HNO_3, 57.8 per cent. acid is present. Since the compound was washed several times with alcohol, the low value for the nitric acid can be readily explained. The probable constitution is $C_2H_6O\begin{matrix}H\\ \diagup\\ \diagdown\\ NO_3\end{matrix}$.

A similar compound, melting at —18°, was made from acetone. The analyses were:

Preparation I: 56.7, 51.0, 50.9
" II: 54.1, 53.8, 53.0 } per cent. nitric acid.

As $C_3H_6OHNO_3$ requires 54.1 per cent. of acid, the constitution is doubtless $C_3H_6O\begin{matrix}H\\ \diagup\\ \diagdown\\ NO_3\end{matrix}$.

Experiments with Sulphuric Acid.—Anhydrous sulphuric acid made from the ordinary and the fuming acid dissolves readily in the cooled organic liquids with evolution of heat. No crystalline compounds were produced, but only syrupy liquids. This is strange, since phosphoric and sulphuric acids[1] give compounds with the much weaker basic substances, phenol and benzoic acid.

Experiments with Chlorsulphonic Acid.—This acid was prepared from sulphuric acid and phosphorus pentachloride and was redistilled; it did not freeze at —80°.

Alcohol instantly decomposed the chlorsulphonic acid, ethyl sulphuric and hydrochloric acids being formed. With ether and acetone white crystalline compounds were obtained, the former melting at —45°, and the latter at —30°. The analytical results were calculated from the total acid found, although the chlorine was also determined. The percentages of acid, in the case of the ether compound, were:

Preparation I: 43.9, 44.3;
" II: 45.8, 46.0;
" III: 42.4, 42.8;

while $C_4H_{10}O$, $HClSO_3$ contains 47.1 and $(C_4H_{10}O)_3$, $HClSO_3$ 34.4 per cent. The probable constitution[1] is:

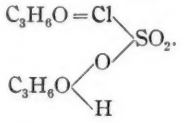
$$C_4H_{10}O=Cl\diagdown\begin{matrix}SO_2.\\ O\\ \diagup\\ \diagdown\\ H\end{matrix}\qquad C_4H_{10}O$$

[1] Hoogewerff and Van Dorp: *Rec. trav. chim.*, **21**, 349 (1902).

The analyses of the acetone compound gave:

Preparation I: 47.3, 47.0;
" II: 48.4, 49.0.

A compound consisting of two molecules of acetone and one of acid has 50.1 per cent. acid, so that the product is $(C_3H_6O)_2,HClSO_3$, and its constitution is:



MacDonald Chemistry Building,
McGill University, Montreal,
May, 1905.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON CHLORONIUM SALTS.

By Julius Stieglitz and Edith E. Barnard.

Received June 12, 1905.

Baeyer's epoch-making investigations[1] on the question of the constitution and the source of color of the triphenylmethane dyes, which grew out of his great work on oxonium salts, have been followed with especial interest by the one of us, because the results promised to throw light on three fundamental questions, in which he has been interested. In 1899[2] attention was called to the necessity of a careful investigation of the question whether the salts of certain carbimide derivatives, such as the imido-esters, are ammonium salts, $R_2C:(NRHX)$, or true salts (not esters or ester salts) of carbon ions $R_2\dot{C}(NH_2)$. All the experimental evidence favoring the latter view, the existence of carbon ions, $R_3\dot{C}$, was suggested and adopted, their formation was supposed to be greatly favored by the presence of imide groups but not limited to imide derivatives[3]. The question, however, is an exceedingly delicate one and physico-chemical measurements carried out since with imido-esters[4] have again raised doubts as to the correctness of the conclusion reached, and we are now inclined rather to the view that the salts are really ammonium salts and

[1] *Ber.*, **35**, 1189, 3013 (1902); **36**, 2774 (1903); **37**, 597, 2818, 3191 (1904); **38**, 569 (1905).
[2] *Am. Chem. J.*, **21**, 101 (1899).
[3] *Loc. cit.*, p. 111.
[4] The results will be published shortly.

that the evidence favoring the existence of carbonium salts may be due to the possibility of tautomeric derivatives, $R_2CCl(NH_2)$ and $R_2C : NH_2Cl$. Since then, the idea of carbon ions, carbon bases and carbon salts has been much more developed and greatly advanced, especially by the work of Gomberg, Kehrmann and Baeyer. The same problem of ammonium (and oxonium) salts *versus* carbonium salts confronted Baeyer and Villiger in the great investigations mentioned above, for instance the problem whether the rosaniline dyes are quinoid ammonium salts $(NH_2C_6H_4)_2$-$C : C_6H_4 : NH_2Cl$ (1), or carbonium salts, $(NH_2C_6H_4)_3C.Cl$ (2), in which the three amide groups simply intensify the positive character of the carbon atom. And, indissolubly connected with this problem is the question whether these dyes owe their color, as hitherto supposed, to the quinoid group in (1) or to the contrast between the positive and the negative groups in (2)—a question in which the theory of indicators[1] is most vitally concerned. The difficulty of reaching a decision in this case as in that of the imido-esters is shown by the fact that the experimental results favored first one view, then the other, but the very fact that Baeyer had the great fact of color to aid him led us to believe that his experimental material would more readily lead to a final decision of the problem than would the colorless carbimide salts under investigation here.

In his latest paper, Baeyer[2] describes most intensely colored salts of trichlor- and triiodotriphenyl carbinol, and the existence of these colored salts has led him to reject the quinoid-ammonium form (1), as representing the constitution of the intensely colored salts of triphenylmethane dyes and to accept and develop that of the colored carbonium salts (2). The salts of the above halogen derivatives do not give a trace of silver halide with silver acetate in glacial acetic-sulphuric acid solutions, even in the course of twenty-four hours. For this reason the quinoid constitution, $(ClC_6H_4)_2C$: $C_6H_4 : \begin{matrix} Cl \\ OSO_3H \end{matrix}$, is rejected and the carbonium constitution, $(ClC_6H_4)_3C.OSO_3H$, accepted. There is, however, another quinoid structure for these intensely colored salts of the halogen derivatives of triphenylcarbinol, a structure which not only restores our confidence in the quinoid theory of color but also suggests to us

[1] Stieglitz: This Journal, **25**, 1112 (1903).

[2] *Ber.*, **38**, 569 (1905).

that Baeyer has most likely made the beautiful discovery of the first well-defined representatives of the long expected class of *chloronium* salts. The structures we would propose are $(ClC_6H_4)_2C : C_6H_4 : Cl.OSO_3H$ and $(IC_6H_4)C : C_6H_4 : I.OSO_3H$ for the chloronium and the iodonium salts, as corresponding to the oxonium salts, $(CH_3OC_6H_4)_2C : C_6H_4 : O\begin{matrix}CH_3\\OSO_3H\end{matrix}$, and to the ammonium salts, $(NH_2C_6H_4)_2C : C_6H_4 : NH_2Cl$.

Basic properties of chlorine have long been anticipated and have been suggested by W. A. Noyes[1], Stieglitz[2], Walden[3] and others. Positive chlorine in such a combination would not readily give silver chloride with silver acetate. Iodonium salts, $R_2I.X$, corresponding to the above assumption, have, of course, long been known, having been obtained, in particular, from phenyl iodides, just as the above salts are derivatives of phenyl halides. The structures suggested are, therefore, not only rational but such compounds have been anticipated with the very properties that Baeyer's beautiful discovery shows them to possess.

In further support of our views we would bring briefly:

(1) The fact discovered by Baeyer that the free imide bases are undeniably quinoids and intensely colored, $(NH_2C_6H_4)_2C:C_6H_4:NR$.

(2) The production of color, as Baeyer repeatedly points out, is intimately connected with the presence of benzene nuclei in a molecule, as is also the power to form quinoid nuclei.

(3) According to the carbonium theory, we must have two different carbinols $(RC_6H_4)_3C.OH$, $(R=CH_3O;\ H_2N;\ Cl;\ I)$, of exactly the same composition and structure, one a true alcohol, that does not ionize to any extent, the other a pronounced base, forming a well-defined salt, which, in the case of a rosaniline, reacts neutral. Such a change of properties without a change of structure or valence ought to be assumed only when all ordinary alternatives fail.

(4) This is likewise true for the acceptance of the same constitution for colorless salts, $(C_6H_5)_3C.Cl$, and intensely colored salts, $(C_6H_5)_3C.Cl,\ SnCl_4$. The color of the latter salts, described by Norris and Sanders, Kehrmann, Gomberg and others, has been

[1] This Journal, **23**, 460 (1901).
[2] *Ibid.*, **23**, 795 (1901).
[3] *Z. physik. Ch.*, **43**, 385 (903).

explained by Kehrmann as being due to their being salts of an isomeric quinoid chloride, $(C_6H_5)_2C : C_6H_4 : \begin{matrix} H \\ Cl,\ SnCl_4 \end{matrix}$; that is, Kehrmann considers them to be carbonium salts of a bivalent carbon base, $(C_6H_5)_2C=C_6H_4<$. It is probable, however, that they are really quinoid chloronium salts, $(C_6H_5)_2C:C_6H_4\begin{matrix} H \\ Cl \\ Cl \end{matrix}SnCl_3$, corresponding to the oxonium salts, $(CH_3)_2O\begin{matrix} Mg—CH_3 \\ I \end{matrix}$, prepared by Baeyer,[1] and to an ammonium or metal ammonium, salt RNH_3Cl. In other words the basic, not the acid, properties of chlorine account for their formation.

(5) Triphenylmethyl chloride is a conductor, especially in acid solvents (sulphur dioxide),[2] and the conducting solutions are colored; the conductivity in acid solvents is as valid an indication of triphenylmethyl chloride being a base—a chloronium base in its quinoid form—as of its being a salt of a carbonium base, as has been argued heretofore. Dimethylpyrone shows exactly the same behavior, forming conducting solutions of oxonium salts in acid solvents.

We do not consider the evidence we have presented as being by any means conclusive but we do believe that our views agree rather better with the facts than does the carbonium theory and that (1) the existence of the long sought chloronium bases will be dated from Baeyer's work and that the endeavor to obtain simpler chloronium salts ought to be undertaken with renewed hope; (2) the quinoid theory of the triphenylmethane dyes should still be maintained; and (3) the existence of true carbonium salts, both in the case of the carbimides and of the triphenylmethane derivatives, is still open to grave doubts.

CHICAGO, June 6, 1905.

NOTE.

The Crystallization of Sodium Iodide from Alcohols.—An accidental observation during the preparation of some ethers by Williamson's method led to the experiments detailed below, which are

[1] *Ber.*, **35**, 1201 (1902).

[2] Gomberg: *Ibid.*, **35**, 2397 (1902); Walden: *Loc. cit.*

merely presented as an addition to the somewhat restricted literature upon the addition products between haloid salts and alcohols.

Sodium iodide is very soluble in absolute methyl alcohol and is not precipitated therefrom upon the addition of a considerable volume of absolute ether, while wet ether produces immediate separation. On cooling a warm solution, rather large plate-shaped crystals separate out, while a solution saturated at room temperature and then cooled below 0°, becomes thoroughly permeated with brilliant white felted needles; although differing markedly in appearance, these two kinds of crystals are identical in composition.

The iodine was determined by Volhard's method; the methyl alcohol, by heating in a current of air and absorbing the vapors in sulphuric acid; the gain in the weight of the latter corresponding accurately to the loss experienced by the crystals. The results agreed very closely with the formula $NaI.3CH_4O$: 38.91 and 38.55 per cent. of methyl alcohol and 51.50 per cent. of iodine. Calculated for $NaI.3CH_4O$, 39.06 and 51.58 per cent.

Potassium iodide, while fairly soluble in alcohol, crystallizes free from it and this seems to be quite a characteristic distinction between the two salts. Sodium iodide crystallizes from ethyl alcohol, forming an addition product, although not quite so readily as with the methyl alcohol. The analysis gave 64.22 per cent. I; calculated for $NaI.C_2H_6O$, 64.91 per cent. This, therefore, seems to be the formula of the addition product with ethyl alcohol.

Normal propyl alcohol dissolves nearly one-third of its weight of sodium iodide and, on evaporation at low temperatures, deposits crystals which appear to have the formula $5NaI.3C_3H_8O$, as two distinct preparations gave 68.26 per cent. and 68.22 per cent. of iodine, against 68.27 per cent. required by theory. Apparently, therefore, the molecular proportion of alcohol assimilated decreases as the series ascends. MORRIS LOEB.

NEW BOOKS.

CONVERSATIONS ON CHEMISTRY: Part I, General Chemistry. By WILHELM OSTWALD. Translation by ELIZABETH CATHERINE RAMSAY. New York: John Wiley & Sons. 1905. vii + 250 pp.

A chemistry in dialogue form without diffuseness, a chemistry vividly up to date, yet within the comprehension of the youngest

pupil, a chemistry hand in hand with experiment and its ungrouped occurrences, yet by ingenious digestion and elaboration organized into a consistent structure, a chemistry in which the common obscurities instead of being handed on in the "original package," according to tradition, are made abundantly plain, all this and far more is Professor Ostwald's latest volume.

The present book contains the first part of the treatise and deals with the application of scientific observation and reasoning to simple physical and chemical phenomena. Substances, their recognition and separation through the use of physical properties, solutions, phenomena of melting, freezing and of boiling, measurement, and state of aggregation are followed by oxygen and combustion. The other materials discussed are hydrogen, water, nitrogen, and carbon and its oxides. At convenient places there are introduced subjects like the conception of elements, the nature of a law and of an hypothesis, the conception of continuity involved in the statement of many laws.

The homely illustrations in the mouth of the teacher and even the school-boy slang of the pupil, which assist materially in holding the attention of the reader, would not harmonize with any other background than that of familiar dialogue which the author has chosen. A discussion as to whether sugar and knitting needles and scissors and paper are all substances closes as follows:

"*Pupil*—Then there are an awful lot of different kinds of substances?

Master—Yes, certainly there are many; far more substances than you can name. And chemistry has to do with all such substances.

P—Oh, then I shall never be able to learn all about chemistry—it's hopeless. I'd rather not begin.

M—Do you know the forest near here?

P—Yes, rather; you could put me where you like in it and I should always know where I was.

M—But you don't know every single tree in it? How can you help being lost?

P—But I know the paths.

M—Now, look here; that is what we are going to do with chemistry. We will not learn every single substance that there is, but we will learn the paths which divide up the countless substances into different groups, and by help of which we can find our way from one place to another. When you know the principal paths

you will know where you are in chemistry, and afterwards you can leave the chief paths and find out more about the by-ways. And you will see that learning chemistry is just as good fun as walking in a wood."

The following, on the possibility of new laws being discovered, is brief enough to quote:

"*Pupil*—Then every one must be able to discover laws of nature?

Master—And so they can, if they find things in conditions not sufficiently discovered. But that is rather difficult, because the common and ordinary conditions of things are already discovered; and it is hard to acquire enough exact knowledge to find undiscovered spheres to examine. For instance, it would be quite easy to discover the north pole if you could only get to it. The difficulty is not to see the North Pole, but to get a place from where it can be seen."

In the preface to the second part Professor Ostwald admits that he wrote not alone for children. If the text-books that we read represent the state of mind of the average chemist then there is not one of them who would not profit immensely if, by reading the book under review, he could catch the sane philosophy, the genial pedagogy, or the rational chemistry in which the dialogues abound.

Miss Ramsay, the translator, may be congratulated on the success with which she has accomplished a task of unusual difficulty.

A. S.

LE FOUR ÉLECTRIQUE. Par ADOLPHE MINET, Paris, 1905, 6 et 12 Rue de La Sorbonne. Price, 5 francs for the first part.

In this volume Professor Minet evidently purposes to give the student of electro-chemistry a very full account of the work possible with an electric furnace. The book will consist of five fasciculi. The first, which is before the reviewer, consists of 72 pages of closely printed matter. The history and development, as well as the classification of electric furnaces, receive pretty full consideration in 11 pages. There then follows a descriptive section of 21 pages in which early laboratory furnaces are discussed, after which there is a pretty full account of the electro-metallurgy of aluminium with reference to the various forms of apparatus used in its isolation. The electro-metallurgy of magnesium, of lithium, of sodium, of potassium and the alkaline earths is discussed. Reference is also made to furnaces of various classes which appeared from the

years 1849 to 1886. The concluding pages of the descriptive part give the bibliography of laboratory furnaces and the various works relating to them. From pages 38 to 72 there is presented an abundance of theoretical matter. As one reads, the impression is received that we have here in a condensed form the most important data for the electrochemist who may be working either in the laboratory or upon a large scale. If this first fasciculus is an indication of what may be expected in the fasciculi yet to appear, the publication of Professor Minet will prove a most valuable and helpful addition to the working library of all electrochemists.

In the second fasciculus is promised a very full discussion of the electro-metallurgy of aluminium, magnesium, glucinum, lead, zinc, etc., together with the electro-thermics of bauxite, quartz; the polymerization of carbon, carborundum, siloxicon, etc.

In the third fasciculus will appear steel, the alloys of iron and a section on alumino-thermics.

The fourth fasciculus will be devoted to phosphorus, arsenic, the chlorides of carbon, carbides, borides, silicides, etc.

The fifth fasciculus will be devoted to general statistics on electric furnaces. It is proposed to bring the subject-matter down to 1906.

The first fasciculus is well illustrated and contains eight portraits of men who have been prominent in the development of electric furnace work. Under each picture is briefly stated the particular line of investigation pursued by the person whose face looks out upon the reader. The eight portraits are of A. Minet, Sir William Siemens, A. K. Huntington, Louis Clerc, W. Borchers, P. Héroult, Alfred H. Cowles and Charles M. Hall.

To American students this work will prove interesting because it shows very clearly the view taken by French electrochemists upon the now rapidly developing and very important field of electro-metallurgy. EDGAR F. SMITH.

A SHORT INTRODUCTION TO THE THEORY OF ELECTROLYTIC DISSOCIATION. By H. C. GREGORY. Longmans, Green & Co. 1905. 76 pp. Price, 1½ shillings.

This is a simple presentation of the subject as confined to aqueous solutions. It first considers the gas laws and the analogies found in these solutions. It briefly refers to osmotic pressure and connects this in the usual way with boiling- and freezing-point effects. The degree of dissociation as indicated by these phenomena is then introduced.

In the second chapter the general principle of precipitation from aqueous solutions as determined by the solubility product and the composition of the ions is discussed, and this in connection with well-chosen illustrations.

Chapter III is devoted to the hydrogen and hydroxyl ions and includes the theory of indicators.

Chapter IV deals with the results of electrolysis of various aqueous solutions as viewed in the light of the dissociation theory. It also includes a treatment of the color produced by ions in solution and general statements as to the dissociation of the different classes of compounds.

The work is a concise and readable treatment of the subject. The choice of method and the experimental illustration are both as well chosen as would be consistent with so brief an introduction to the theory. W. R. WHITNEY.

PRACTICAL METHODS OF ELECTRO-CHEMISTRY. By F. MOLLWO PERKIN, PH.D., Head of the Chemistry Department, Borough Polytechnic Institute, London. New York: Longmans, Green & Co. 1905.

The present volume does not pretend to give a complete course in practical electro-chemistry. It gives examples in the determination of metals and also in their separation. It also gives a very good list of examples in inorganic and organic electro-chemistry. To have made it representative there should have been added experiments with the electric furnace.

The introduction of the book contains a number of very interesting points for the beginner in electro-chemistry. They have been set forth very clearly and certainly will prove helpful to those who are about to take their first step in this growing department of chemistry. It is right and proper that the author should emphasize the important points in the work of Michael Faraday. Those who are acquainted with the subject well know that he truly deserves the title of "Father of Electro-chemistry;" but, in these days there is a tendency—not intentional be it said—to ignore much of the work that we owe to that great master.

The writer's experience would lead him to differ as to the value of some of the methods suggested for the determination of the few metals which are given, and also, to some of the separations. For example, the author of the book seems to think that the old gravimetric method for the separation of silver from copper is preferable to any electrolytic procedure. This certainly is not correct,

for any one who has interested himself in the separation of these two metals in a cyanide solution well knows that the current separates them most completely and in the most satisfactory form; that little is left to the analyst himself and the results are reliable and accurate.

A curious mistake is made by the author in the section entitled "Metals Deposited as Oxides at the Anode," where one reads, for example, that uranium is deposited as the hydrated oxide U_3O_4, page 141, and molybdenum as hydrated sesquioxide, page 142, *on the anode*. Perhaps this is a slip on the part of the author; but it is one to which his attention should be called. The hydrated oxides, just referred to, are deposited quantitatively *upon the cathode*. There are, also, several names of chemists improperly or incorrectly spelled (Muir for Muhr page 127, and Korn for Kern page 141, etc.,); but this will be corrected, no doubt, in a subsequent edition.

One would think that in a book which has appeared so recently some mention would be made of the latest developments in electro-analysis. It is true that in speaking of the forms of apparatus used in work of this kind brief mention is made of a suitable rotating cathode, and that Gooch and Medway used a platinum crucible for this purpose; but the strangeness is that the student is not told how easily most of the metals are determined to-day by rotating the anode. When it is possible to make a determination of copper, precipitating as much as 0.5 gram in weighable form in from five to ten minutes—a thing that is being done daily —it would seem that some directions might be given the student to do this; and that when it is possible to analyze completely a nickel coin, or even determine the zinc in sphalerite in a period of time not exceeding two hours, that those who are expected to do work in practical electro-chemistry should have received a hint as to how these rapid determinations may be carried out. It is not necessary to refer to the absence of any allusion to the use of a mercury cathode; yet, as these new things have been so rapidly and beautifully confirmed by experiment they deserve a passing notice.

The section devoted to the preparation of inorganic and organic compounds is superior to that devoted to the analytical processes, and students will carry out the experiments there described with a great deal of satisfaction.

The volume aims apparently to bring together in a concise form the striking features of books like Oettel's "Electrochemical Experiments," Oettel's "Exercises in Practical Electro-chemistry," Elbs' "Electrolytic Preparations," and those of the various books on electro-analysis. The author states in his preface that he had in view the making of a book which should stimulate experimentation in the great field of electro-chemistry. His effort will be helpful, and deserves a place among the many other books which have been written at various times and in different lands for the same purpose. As a student of electro-chemistry the writer feels himself indebted to Dr. Perkin for this contribution.

EDGAR F. SMITH.

LEÇONS SUR LA THÉORIE DES GAZ. PAR LUDWIG BOLTZMANN. Traduites PAR A. GALLOTTI ET H. BÉNARD. Seconde Partie. Paris: Gauthier-Villars. 1905.

The author notes that since the publications of the first part of the present work many objections against the kinetic theory of gases have appeared, but he is convinced that the objections rest solely on misunderstandings, and that the theory is to render further services to science. He gives many pages to the wealth of deductions from the theory which were obtained by van der Waals, and which have been found to agree with experience; and tells how Ramsay used the teachings of the theory in determining the atomic weight of argon and its place in the periodic system of the elements, and how after the discovery of neon good ground was afforded for accepting the number assigned to argon. He thinks it would be a disaster to science if any weight of authority arrayed against the kinetic theory should cause it to fall into temporary oblivion, as the authority of Newton caused the undulatory hypothesis to fall.

The topics considered in this second part are three: The theory of van der Waals, polyatomic gases and dissociation. The object here, as in the first part, is to examine, by rigorous mathematical methods, the consequences of certain hypotheses. Such a discussion, somewhat remote from chemistry and even from physical chemistry, leans so far towards mathematical physics that a journal of chemistry must mention it but briefly. It is the great work of the leading exponent of the kinetic theory on its mathematical side, and this clear translation into French will facilitate its study.

EDWARD W. MORLEY.

LABORATORY NOTES ON PRACTICAL METALLURGY. By WALTER MACFARLANE. New York: Longmans, Green & Co. x + 40 pp.

This book is designed to be a graduated series of exercises leading up to the various metallurgical processes. It begins with the melting and pouring of metals and alloys, gives experiments in cupellation, scorification and liquation; the reduction and fusibility of silicates; the assay of silver and gold ores; and the analysis of fuels.

There seems to be much duplication of experiments all illustrating the same principle, especially in the first part of the book, many of which might have been performed in an elementary course in chemistry. The directions are all detailed, but this is probably necessary in an elementary book. The interpretation of results is left entirely to the student and with proper guidance from the instructor should lead to valuable results, especially so since the experiments are logically arranged.

The melting-points of the metals given on page 123 do not give the most recent values, and in the case of manganese is distinctly wrong, giving 1900° instead of the Heraeus value of 1245°.

HENRY FAY.

A LABORATORY CHEMISTRY. By RICHARD B. MOORE, Instructor in Chemistry, University of Missouri. Philadelphia and London: J. B. Lippincott Company. 1904. 194 pp.

The author of this book is of the opinion that the chief weakness in the training of students of elementary chemistry in the secondary schools is a lack of drill in the scientific method, and an almost entire neglect of the theoretical principles which underlie the science. He has emphasized, accordingly, in this book the more important theories of inorganic chemistry and the physical principles underlying these theories. Almost one-half of the book is devoted to a consideration of that part of physics which the teacher of chemistry is called upon to use. The following subjects are treated at some length: Units of Measure, Specific Gravity, Measure of Length, Expansion of Solids, Liquids, and Gases, Charles' Law, Boyle's Law, Barometer, Change of State, Boiling-point, Freezing-point, Effect of Dissolved Substance on Boiling-point, Specific Heat, Latent Heat, and Electrolytic Dissociation. The chapters give a clear exposition of the principles and contain laboratory directions for experiments which serve to illustrate the principles discussed.

The atomic theory, valency, and the quantitative relations between the weights of substances which enter into a chemical reaction are discussed in a very satisfactory manner, and are illustrated by a number of appropriate experiments. The last chapters contain directions for a few of the experiments usually found in the laboratory guides in chemistry.

The book will be helpful to the large number of teachers who, unfortunately, are compelled to teach chemistry to students who have had no training in physics. JAMES F. NORRIS.

METALLURGY OF CAST IRON. A complete exposition of the processes involved in its treatment, chemically and physically, from the blast-furnace through the foundry to the testing machine. A practical compilation of original research. By THOMAS D. WEST. Fully illustrated. Ninth edition. Cleveland, O.: The Cleveland Printing and Publishing Co. Price, $3.00.

That there has been a real need for a comprehensive treatise on this subject and that it has been met by the book under consideration are evidenced by the issue of nine editions in as many years.

It aims to present in as plain a way as possible the principles of the smelting of iron ores and the treatment of cast iron in the foundry, together with a discussion of the constitution of the various grades of iron, the appearance of its fracture as related to the chemical composition and the physical effects of impurities normally or occasionally present. A considerable part of the book is devoted to the mechanical testing of sample bars, and the effects of heat and mechanical treatment are discussed at length. Many of the original investigations of the author and his associates in this field are here recorded.

The book can be commended to all those interested in the production or use of cast iron as being both modern and free from unnecessary technicalities. FRANK JULIAN.

EXPERIMENTAL RESEARCHES ON THE CONSTITUTION OF HYDRAULIC MORTARS. By HENRI LECHATELIER. Translated by JOSEPH LATHROP MACK. New York: McGraw Publishing Co. Cloth. 12mo. 140 pp. Price, $2.00.

Mr. Mack has put all persons who do not read French under obligation by his translation of the thesis of Le Chatelier "On the Constitution of Hydraulic Cements," which was presented by him for the Degree of Doctor of Science before the Faculty of Sciences

of Paris, on July 6, 1887, and which Le Chatelier republished in a second edition in 1904 together with several papers of later date, owing to the fact that the earlier publications were not generally available. This thesis, as Le Chatelier states in the preface to the second edition, has been the foundation for much subsequent work and it is classical in its importance, many of his conclusions having been confirmed by more recent investigations.

Mr. Mack's translation is a clear one and should be in the hands of everybody who is interested in the subject. It is to be regretted that he did not include the papers forming the fourth part of the second edition of 1904, all of which are of interest.

CLIFFORD RICHARDSON.

THE MODERN ASPHALT PAVEMENT. By CLIFFORD RICHARDSON. New York: John Wiley & Sons. Cloth. 8vo. Price, $3.00.

Mr. Clifford Richardson's book, "The Modern Asphalt Pavement," is by far the fullest treatise that has been published on the subject and is the first book that discusses the details of this industry. Without doubt, it will do much toward accomplishing what the author states in his introduction is the object of the work: "To demonstrate the nature of asphalt pavements and the causes of defects in them, to bring about improvement in the methods of their construction, and to show how this can be done."

The book, with the exception of one short chapter on asphaltic concrete, deals exclusively with the modern sheet asphalt pavement, the materials and the methods of construction, some views as to the cause of their failure and the methods of examining the materials used. The materials and methods of construction described, as is natural to expect owing to the author's present connection with the Trinidad Asphalt interests, are those principally applicable to this asphalt. While they are applicable in a degree to other brands of asphalts it is to be regretted that Mr. Richardson does not discuss a little in detail the modifications that are desirable with different asphalts.

The book is divided into parts, each treating of the different branches of the industry, while chapters give the details.

Parts 1, 2 and 3 discuss and describe in a general way the various parts of an asphalt pavement and describe the various materials used in the construction of these parts. Chapters III and IV

discussing the mineral aggregate and filler is one of the fullest and most lucid dissertations that has been written on this much neglected subject of sands and will prove interesting and instructive not alone to those interested in paving, but to engineers in general. Chapter XVI on the technology of the asphalt surface mixture should be read in conjunction with the above-mentioned chapters, as it discusses paving mixtures met with in practice and the relation of their behavior to the mineral aggregate they contain. It, however, should be treated more as a study than as a guide for the actual construction of a pavement, for, while the author apparently recommends, for all cases, what he calls his "standard sands," yet he admits that different sands, even of the same mesh composition, act differently owing to the character of the grain. It must be borne in mind, also, that asphalts with different physical properties require different sands; and that different streets, depending on the extent and character of traffic, require different sands. In Chapter V the author gives an elementary talk on the molecular construction of hydrocarbons intended as an aid for those not acquainted with chemistry.

In Part 3 the author takes up the discussion of the different asphalts and bituminous materials used in the paving industry and gives tests on the same.

It is to be regretted that the subject of bitumens as presented in this part of the book is dealt with so poorly, as it is the branch of the industry least familiar to the general profession. There are many misleading statements and discussions all through this part, and that the asphalts were treated with such inadequate justice can possibly only be explained by the fact that the author's long connection with the Trinidad Asphalt interests has made him more familiar with this material than the others. A few of the statements on the asphalts, drawn from either unreliable or inaccurate premises, are as follows: He states the difference between Trinidad Land and Trinidad Lake Asphalt are brought out by the fact that where 20 pounds of residuum are sufficient to make an asphalt cement when added to 100 pounds of Lake Asphalt, as much as 30 or more pounds of the same residuum are required to make a cement of the same consistency with Land Asphalt. This statement is not substantiated by the facts. The difference on an average is 5 pounds of residuum to 100 of asphalt.

On page 194 the author, in speaking of the asphalt on the More

Ranch, California, says: "This deposit of asphalt is of importance not on account of its size, but because the addition of perhaps a shovelful of it to each barrel of residual pitch has been used as a basis for the statement that the latter contains a native solid bitumen." The author so far forgets himself in this case as to state as a fact in a book which is supposed to be instructive a trade argument used by an asphalt company against a competitor. It is doubtful whether absolute proof of his above statement is obtainable, as there is sufficient evidence to the contrary to make it at least debatable, and even though he possessed absolute proof it ought hardly find place in a book such as this.

And still another case on page 236, in speaking of the bituminous sands of Santa Barbara County, Cal., he says: "The bitumen which these sands contain is in the form of maltha . . . . ." In this he is mistaken. In all of the mines mentioned the bitumen is more or less soft but not maltha. The author has failed to mention the "New Mine" which is about 100 yards to the northwest of the Side Hill Mine and from which a hard material is obtained for mixing with the softer. The bitumen of this material is about as hard as that of Trinidad and by proper blending it is possible to obtain a pavement similar to any that can be produced by artificial means. Alluding to the pavements of this material in San Francisco the author says: " . . . . . there is now a tendency to abandon this form of asphalt pavement and to construct surfaces from properly graded sand combined with filler and a suitable pure bitumen." It is not two years since the reviewer called on the city engineer and the asphalt chemist of San Francisco and looked over the pavements with them. They expressed the opinion that the bituminous sand pavements were superior to the artificially mixed ones.

In Chapter XIII Mr. Richardson associates together indiscriminately carefully prepared asphalts from California oils and residues of oil refineries and from the examination of this heterogeneous collection he draws the conclusion that asphalts made from California oil are not uniform and, as a rule, unsuitable for paving purposes. Yet good pavements made from this material are met with in many cities with climates ranging from that of Winnipeg, Manitoba, to that of Southern California.

There are many more instances that might be pointed out, though of less marked degree, of the author's seeming partiality.

Parts 4 and 5 are devoted to the technology of the paving industry. The former discusses the manufacture and preparation of the material at the paving plant; the latter, the laying of the materials on the street. In these two parts is the best description of the technology of the paving industry that has been published and will without doubt, when carefully read, prove of considerable value.

Part 6 is a discussion of the physical properties of asphalt surfaces. The author here discusses radiation, expansion, contraction and the resistance to impact.

Part 7 treats of specifications and merits of asphalt pavements. The last chapter of this part relates to the action of water on asphalt pavements. The author stands practically alone among many experimenters in the interpretation of laboratory tests in this respect. Fig. 21, showing the action of running water on three different asphalt cements, is misleading, as the defects that can be noticed in the cut can not be the result of rotting or disintegration after so short a period of exposure to the action of water, but are due to physical deformities resulting from the flowing of the water over the samples. The value of the author's tests in exposing cylinders of asphalt mixture to water is detracted from by the samples being burnished from time to time, as described on page 439. This, of course, prevents the action of water on the cylinder in the laboratory, but has no bearing on what takes place on the street where water attacks a pavement from underneath and other portions not exposed to the burnishing action of traffic.

Part 8 is on the causes of the defects in and the deterioration of asphalt surfaces. As the author in all his conclusions fails to differentiate between the action of water on different asphalts the value of this part is unfortunately largely detracted from.

Part 9 is well worthy of consideration, as it emphasizes the importance of the control of the work by laboratory examinations. The author goes into the subject in detail of how samples should be collected and describes the methods employed in his laboratory for their examination.

The book, if carefully read, is a valuable contribution to the literature on this subject, but the reader should not accept the dogmatic statements of the author on the many debatable points, and should always keep in mind the author's point of view.

ALLAN W. DOW.

FRICTION AND LUBRICATION. A HANDBOOK FOR ENGINEERS, MECHANICS, SUPERINTENDENTS AND MANAGERS. By WILLIAM M. DAVIS. Second Edition, Illustrated. Pittsburg, Pa.: The Lubrication Publishing Co. 1904. 8vo. 265 pp.

This work considers the subject from the practical or mechanical point of view and, being intended more particularly for the classes of men noted on the title page, is presented in a plain and concise way. The subject is one, as the author notes, which has not received the attention that it deserves or that it would pay to give it.

The subjects treated embrace those of friction and friction losses, the theory of lubrication and the lubrication of different varieties of machinery, as engines of all kinds, mining, refrigerating, textile, flour mill, compressed air, steel works, machinery, cars, etc., etc.; particular attention being paid to cylinder and valve oiling. Bearings, journals and bearing metals receive considerable attention, as do also the testing and properties of the various oils and greases. Oiling devices and a chapter upon oil house methods, oil storage and gauging complete the volume.

The book fills a long-felt want and the reviewer knows of no other treatise in which the difficulties incident to lubrication, as the groaning of valves, the cutting and scoring of cylinders and the various experiences with all sorts of lubrication are so fully and ably considered. The method described for the determination of the percentage of animal or vegetable oil in a compound oil, as described, would give high results, due to the fact that the ether solution of the petroleum oil contains soap not having been washed with water.

The work is a most excellent one and may be recommended to every one having to do with oils. A. H. GILL.

PERCENTAGE TABLES FOR ELEMENTARY ANALYSIS. By LEO F. GUTTMANN, PH.D., A.C.G.I., A.I.C. London and New York: Whittaker & Co. 1904. 43 pp.

This book gives tables for calculating the percentages of carbon and hydrogen in organic combustions. There are, besides, a table of proportional parts for use in interpolating and a table giving the weight of a cubic centimeter of moist nitrogen at different temperatures and pressures. The latter is based upon Dietrich's table,[1] and the values given are, therefore, about 0.50 per cent. higher than they should be for "chemical" nitrogen.[2] The tables

[1] *Z. anal. Chem.*, **5**, 36 (1866).

[2] Rayleigh and Ramsay: *Z. physik. Chem.*, **16**, 346 (1895.)

will be found very useful in laboratories where many organic combustions are made. C. E. WATERS.

THE NEW KNOWLEDGE A POPULAR ACCOUNT OF THE NEW PHYSICS AND THE NEW CHEMISTRY IN THEIR RELATION TO THE NEW THEORY OF MATTER BY ROBERT KENNEDY DUNCAN New York 1905

Our lately acquired knowledge of the phenomena of radioactivity is now so considerable that a popular summary of the whole subject is very desirable. The author of this book, who says that "the world is divided between men who know and cannot tell and men who tell and cannot know," has attempted to supply this desideratum, justifying the attempt, "because of the need of some interpretation of this new and interesting knowledge, and because of his own sincerity.

The work is much to be commended to those for whom it has been written; that is, to teachers who have no convenient access to the original papers of numerous scientific journals, to students and those who have been students, and to the general public. It contains a clear and orderly statement of the facts of radioactivity so far observed, as well as of some related and longer known facts needed in the discussion of the former.

Part First is entitled "Current Conceptions;" it concludes with definitions of the terms *compound*, *element*, *molecule*, and *atom* such as have been received for half a century. The succeeding five parts treat of "The Periodic Law," of "Gaseous Ions," of "Natural Radioactivity, a New Property of Matter," of the "Resolution of the Atom," and of "Inorganic Evolution."

They well state observed facts and the more special theoretical conclusions suggested by them. The concluding seventh part is entitled "The New Knowledge and the Old Problems," and states the more general theoretical conclusions. It discusses the source of the sun's heat, the age of the earth, the nature of the tails of comets, solar prominences and the solar corona, the zodiacal light, the aurora borealis, and the possible reconstruction of a universe which shall have become extinct by losing all its available energy. In one chapter of this seventh part, the terms defined in the first part are defined anew in a way which well sums up the recent increase of our knowledge and the wealth of fruitful and useful conjecture derived from it. Such conjectural conclusions are carefully represented as tentative and provisional, and it will not be the fault of the author if some recent hypotheses are accepted

by the less careful with a confidence somewhat in inverse proportion to their present probability.

Errors of fact are few. The author says of the amount of radium yet obtained, "as a matter of fact, not much more than a gram exists." This is an understatement. He says of a recent paper by Mendeléeff, "On this hypothesis, Mendeléeff accounts fairly well for the properties of the ether." Mendeléeff himself would scarcely claim to have explained how a gas can convey transverse vibrations; until this is accomplished, the hypothesis in question cannot fairly be said to *begin* to account for the properties of the ether.

The author recognizes that he may be thought somewhat enthusiastic; there are some exuberant expressions, reminding one of a photograph made with a lens of extreme wide angle, and some epigrams on subjects too complex for the combination of epigram with justice, like the first phrase quoted above. Facts are well stated, and the balance between facts and more or less uncertain inferences is held with steady hand, while these inferences, most interesting, although uncertain, are adequately presented. The book ought to be received with much favor, and is heartily commended to all readers of our journal. EDWARD W. MORLEY.

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